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XLVIII.—ON THE DIRECT CONVERSION OF AROMATIC SULPHONATES INTO THE CORRESPONDING AMIDO COMPOUNDS.[1]

BY C. LORING JACKSON AND JOHN F. WING.

The action of sodium or potassium amide on organic substances has been studied but little; in fact, when we took up the subject, there were no papers more recent than those of Beilstein and Geuther[2] on sodium amide in 1858, and of Baumert and Landolt[3] on potassium amide in 1859. The reason for this neglect may be found probably in the curious observation made in both of these papers, that the alkaline amides are not acted on in the way which we should expect by most haloid organic compounds, neither ethyl chloride nor iodide, nor chlorbenzol nor acetyl chloride, giving the corresponding amido compounds;[4] in fact, benzoyl choride is the only haloid organic compound tried which acted as would be

[1] From the Proceedings of the American Academy of Arts and Sciences. Communicated by the authors. [2] Ann. Chem. **108**, 88. [3] *Ibid.* **111**, 1.

[4] These results, so far as the ethyl compounds are concerned, have been confirmed recently by J. Walter, who, in a paper (Journ. pr. Chem. **34**, 132) drawn out by the preliminary notice of our work, states that at low temperatures no ethylamine is formed from ethyl bromide; but by heating the sodium amide until it begins to melt, and passing over it a stream of hydrogen impregnated with ethyl bromide, ethylamine was formed, recognised by the carbylamine reaction. Under similar conditions brombenzol gave small quantities of aniline. He, however, does not consider it proved that the amine was formed from the sodium amide, rather than from the ammonia set free during the reaction.

expected, giving benzamide and dibenzamide. Accordingly, in taking up the subject, we have turned our attention to the effect of sodium amide on sulphonates, in the hope of obtaining an action similar to the well-known replacements of the sulpho-group by hydroxyl, cyanogen, or carboxyl, when fused with potassic hydrate, cyanide, or formiate respectively. This expectation has been fulfilled, as by heating potassic benzolmonosulphonate with sodium amide we have obtained aniline, and in the same way metaphenylenediamine from potassic benzolmetadisulphonate; but, unfortunately, the yield, especially in the latter case, is so small that the method could hardly be used with profit for the preparation of new amido compounds, so that its usefulness must be confined to determinations of constitution.

The sodium amide was prepared according to the method of Beilstein and Geuther—that is, passing dry ammonia gas over sodium heated in a series of small flasks—except that after the first experiment we dispensed with the use of hydrogen for expelling the air from the flasks before the sodium was heated, using the ammonia gas itself for that purpose.

Action with Potassic Benzolmonosulphonate.—One of the flasks containing the sodium amide was broken, its contents pulverised as rapidly as possible, and mixed (without separating the powdered glass from the flask) with anhydrous potassic benzolmonosulphonate in about the proportion of one molecule of each, calculated from the amount of sodium used in making the amide. The mixture was then heated gently over the lamp in a test tube until the brown fused spots which appear at first had spread throughout the entire mass; but the process should be stopped before these spots show signs of decomposition, as, if the heat is carried too high, the yield is not so large. During the heating some aniline vapor escapes, but the amount of this is so insignificant that it is not worth while to carry on the process in a retort. The product was then carefully treated with water, and distilled with steam as long as anything passed over. The presence of aniline in the turbid distillate was determined by its smell, by the strong purple color which the distillate gave with a solution of bleaching-powder, and by the analysis of the chloride made by adding dilute hydrochloric acid to the distillate, filtering and evaporating to dryness.

0.4966 gram of the salt gave 0.554 gram of argentic chloride.

	Calculated for $C_6H_5NH_2Cl$.	Found.
Chlorine	27.41	27.60

The yield varied a great deal, but was in the neighborhood of 10 per cent., rising once as high as 15 per cent. of the theory. The portion of the distillate insoluble in dilute hydrochloric acid consisted of white scales, which, after repeated recrystallisation from ligroine, melted between 53° and 54°, and gave an intense blue color with strong nitric acid. We therefore inferred that they consisted of diphenylamine, an inference confirmed by the analysis of the chloride prepared by the action of strong hydrochloric acid and alcohol on the substance, which gave the following result:

0.1334 gram of the salt gave 0.0916 gram of argentic chloride.

	Calculated for $(C_6H_5)_2NH_2Cl$.	Found.
Chlorine	17.27	16.97

The formation of diphenylamine by this reaction would seem to show that the sodium amide used by us was a mixture of $NaNH_2$ with Na_2NH, whereas Beilstein and Geuther proved that the formula of their sodium amide was $NaNH_2$. The explanation of this difference probably can be found in the fact that our amide still contained an excess of sodium, the flasks used by us not being made of a sufficiently resistant glass to allow us to carry the reaction to an end, while in their experiments all the sodium was converted into the amide. It is also possible, but not probable, that the diphenylamine was formed by a secondary reaction from the aniline.

Some experiments to determine the temperature at which the reaction takes place showed that some amine was obtained at 280°, and the yield was not improved at 300°–350°; but that a much better result was reached by heating over the free lamp than with an oil or air-bath, the products at the temperatures given above amounting respectively to 6.8 and 5.4 per cent. of the theoretical, or about one-half of the amount obtained by the more rapid direct heating over the lamp.

Action of Potassic Benzolmetadisulphonate.—The salt, mixed with about the equivalent amount of sodium amide, was heated in a test tube as before; but it was found necessary in this case to continue the heating until the brown spots which formed at first had turned black and showed signs of decomposition, since, if the action was stopped while they were still brown, as in the case of the monosulphonate, the yield was exceedingly small. At best,

the yield was not satisfactory, reaching at the outside five per cent. of the theory, so that we did not attempt to collect enough of the tolerably unstable chloride of the metaphenylenediamine for analysis, but contented ourselves with proving its presence by qualitative tests. For this purpose, the product of the reaction was cautiously treated with water, and the aqueous solution extracted with ether; one portion of the ether extract was shaken with dilute sulphuric acid, and to the acid solution thus obtained a very minute amount of sodic nitrite was added, which turned it yellow; another portion of the ether extract was shaken with dilute hydrochloric acid, the acid solution evaporated to dryness, and the residue redissolved in water, filtered from brown decomposition products, and treated with a solution of sodic nitrite, when a heavy, reddish-brown precipitate of phenylene brown was formed; finally, another portion of the ethereal solution of the base was treated with a solution of the nitrate of diazobenzol, when a red, crystalline precipitate was formed, which turned yellow upon the addition of ammonic hydrate, and was therefore the nitrate of chrysoidine. All these tests indicate the presence of metaphenylenediamine in the product of the action of sodium amide upon the potassic benzolmetadisulphonate. The small yield is undoubtedly due to decomposition of a portion of the diamine at the comparatively high temperature necessary for the reaction, as there was a large amount of tarry matter always associated with the product.

XLIX.—ON BENZYLDIMETHYLAMINE.

By C. Loring Jackson and John F. Wing.

At the beginning of the last academic year we prepared the benzyldimethylamine with the intention of making an extended research on this substance; but as the carrying out of this research has been indefinitely postponed on account of the pressure of other more interesting work, we have thought it proper to publish the results already obtained, consisting of the preparation and properties of the base and some of its salts, for the benefit of any one who may follow us in this line of research, rather than on account of any especial interest in the results themselves.

The benzyldimethylamine has been already obtained by Schotten,[1] as one of the products of the distillation of the free base derived from the addition product of methylbenzylpiperidine and methyl-iodide; but he contented himself with the determination of its presence by the analysis of its chlorplatinate.

Benzyldimethylamine.—To prepare the substance an alcoholic solution of dimethylamine was made by the decomposition of nitrosodimethylaniline, according to the method of Baeyer and Caro,[2] the gas being passed into absolute alcohol, and this was allowed to stand for some hours with benzylchloride. At the end of this time the reaction, which was accompanied with evolution of heat, was finished; and after distilling off the alcohol on the water-bath, the product was treated with water, and then with hydrochloric acid, after which it was extracted with ether to remove a slight non-basic impurity. The base was then set free with sodic hydrate, extracted with ether, washed in the ethereal solution, dried with potassic hydrate, and purified by distillation after driving off the ether. The aqueous liquid, from which the base was extracted with ether, contains the excess of dimethylamine, and the chloride of dibenzyldimethylammonium, the extraction of which will be described later in this paper.

Properties of the Benzyldimethylamine.—It forms a colorless liquid with a peculiar smell, boiling at 183°–184°[3] with the column entirely in the vapor and the barometer at 76.53 cm. It is insoluble in water, but mixes freely with alcohol or ether. Two attempts to convert it into a nitroso-compound gave negative results.

The *chloride* is deliquescent, and forms white, radiating crystals.

The *nitrate* is also deliquescent, so that crystals can be obtained only with difficulty; it forms slender white needles, with many shorter ones crossing them at right angles.

The composition of the base was determined by the analysis of its chlorplatinate and acid ferrocyanide.

Chlorplatinate, $[C_7H_7(CH_3)_2N]_2H_2PtCl_6$.—The salt was prepared by adding chlorplatinic acid to the free base, purified by crystallisation from water, dried at 100°, and analysed.

[1] Berichte d. deutschen chem. Gesellschaft **15**, 424.

[2] *Ibid.* **7**, 963.

[3] This determination of the boiling-point was made with too small a quantity of the substance, and must be considered as merely approximate. If we had continued the research, we should have repeated it on a more satisfactory scale.

I. 0.2288 gram of the salt left on ignition 0.0656 gram of platinum.
II. 0.3320 gram left 0.0944 gram of platinum.
III. 0.3994 gram left 0.1148 gram of platinum.
IV. 0.4244 gram left 0.1216 gram of platinum.

	Calculated for $[C_7H_7(CH_3)_2N]_2H_2PtCl_6$.	Found. I.	II.	III.	IV.
Platinum	28.63	28.67	28.43	28.74	28.65

Properties.—The appearance of the substance varied a great deal, according to the conditions under which the crystals were obtained; thus, we have observed it in thick orange prisms, in long yellow needles, or in pointed crystals shaped like a spear-head.[1] It is slightly soluble in water and in alcohol. Water is the best solvent for it, good crystals being easily obtained from the aqueous solution.

Ferrocyanide, $(C_7H_7(CH_3)_2N)_2H_4Fe(CN)_6$.—This substance was obtained as a white precipitate, when a solution of potassic ferrocyanide was added to a slightly acid solution of the chloride. It contains no water of crystallisation, and its composition was determined by the following analyses:

I. 0.5224 gram of the salt dried in vacuo gave on ignition 0.0852 gram of ferric oxide.

II. 0.3714 gram gave 0.0612 gram of ferric oxide.

	Calculated for $[C_7H_7(CH_3)_2N]_2H_4Fe(CN)_6$.	Found. I.	II.
Iron	11.53	11.41	11.53

Properties.—It forms white, pearly scales, which are very sparingly soluble in water, and on exposure to the air turn slightly green, but the amount of the decomposition thus indicated is so small as to be inappreciable by analysis.

With mercuric chloride the base gave an uninviting, viscous product, while with zincic chloride it formed a characteristic double salt, which separated from concentrated solutions as an oil, but soon solidified in good-sized rhombic crystals; an analysis of a not perfectly pure sample of this salt led to the following results:

0.3492 gram of the salt gave 0.4090 gram of argentic chloride.

	Calculated for $[C_7H_7(CH_3)_2NHCl]_2ZnCl_2$.	Found.
Chlorine	29.65	28.95

Dibenzyldimethylammonic Chloride, $(C_7H_7)_2(CH_3)_2NCl$.—This substance was left in the aqueous solution after the benzyldimethyl-

[1] The identity of the substance in all these forms was proved by analyses.

amine had been shaken out with ether, and, when this solution was evaporated to one-half its original volume, separated as a yellow oil, which solidified as it cooled. It can be freed partially from the inorganic salts present mechanically, or by solution in chloroform, although chloroform does not remove it from its aqueous solution, and purified by washing with a saturated solution of sodic carbonate, and finally dissolving it out of the inorganic impurities with alcohol or chloroform.

Properties.—It forms white rhombic crystals, often in spear-head forms and a centimetre broad, or masses of radiating prisms or needles, but usually separates from its solutions as an oil, which solidifies after standing for some time, more rapidly if touched with a crystal of the substance. It is freely soluble in water, but nearly insoluble in a saturated solution of sodic carbonate, soluble with some difficulty in alcohol, but freely in chloroform, which is the best solvent for it; it is also soluble in ether, benzol, carbonic disulphide, and glacial acetic acid, insoluble in ligroine. When heated, it gives benzylchloride, recognised by its smell and its action on the eyes, and a base, which, however, seems to boil at a higher temperature than the benzyldimethylamine; but the experiment should be repeated on a larger scale. If the aqueous solution of the chloride is boiled with argentic oxide, it becomes strongly alkaline, but it is necessary to boil for some days in order to convert it completely into the free base.

Dibenzyldimethylammonic Chlorplatinate, $[(C_7H_7)_2(CH_3)_2N]_2PtCl_6$.—This substance was prepared by adding an alcoholic solution of the chloride to chlorplatinic acid, and purified by recrystallising from water. Its composition was determined by the following analysis:

0.2012 gram of the salt gave 0.0454 gram of platinum.

	Calculated for $[(C_7H_7)_2(CH_3)_2N]_2PtCl_6$.	Found.
Platinum	22.64	22.56

It is nearly insoluble in cold water, but crystallises from a hot aqueous solution in large, shining, yellow plates often a centimetre in length, or in feather-like forms.

L.—A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF HYDROXYL.

By C. Loring Jackson and G. W. Rolfe.

The methods now in use for determining the number of hydroxyl radicals in a molecule can be divided into two classes—those which consist in the analysis of the acetyl or benzoyl compound, and those which depend on the saponification of the acetyl compound and the quantitative determination of one or other of the products of the decomposition. Methods of the first class cannot be applied to substances having large molecular weights, as then the differences in percentage composition approach the limit of error of the analysis; and even methods of the second sort have led to false conclusions in many cases (for instance, with æsculine and æsculetine, which give soluble compounds with magnesic hydrate), or are inapplicable, owing to the instability of the compound with saponifying agents. We have worked out, therefore, a new method for determining hydroxyl quantitatively, which is applicable in cases where the methods now in use can be applied only with difficulty or give uncertain results, and, we hope, will commend itself also in other cases on account of its simplicity, as it does away with the additional operation of saponification—often a tedious one—necessary in methods of the second class.

Our process consists in converting the substance into its parabrombenzoyl compound, and determining the amount of bromine introduced by an analysis according to the method of Carius. It therefore belongs with methods of the first class, but has the advantage that the differences in percentage composition are larger than when carbon and hydrogen are determined in the benzoyl or acetyl compounds, as is shown by the following comparison of the differences caused by the presence of one more hydroxyl in the molecule between the percentages of carbon in the benzoyl and of bromine in the brombenzoyl derivatives of æsculetine, æsculine, and fisetine,[1] substances which we have selected for calculation on account of the differences in their molecular weights.

Name and Formulas of Substance.	Benzoyl Compound. Difference in percentage of C.	Brombenzoyl Compound. Difference in percentage of Br.
Æsculetine, $C_9H_3O(OH)_3$ / $C_9H_4O_2(OH)_2$	1.97	3.60

[1] Schmid, Berichte d. deutsch. chem. Gesell. **19**, 1351.

Æsculine, $C_{15}H_{10}O_3(OH)_6$ / $C_{15}H_{11}O_4(OH)_5$	0.90	1.50
Fisetine, $C_{23}H_{10}O_3(OH)_6$ / $C_{23}H_{11}O_4(OH)_5$	0.78	1.66

The numbers given in the third column of the above table are far enough removed from the maximum analytical error to leave no doubt in regard to the composition of the substance; and we may add that, as far as our experiments go, the parabrombenzoates show a much greater tendency to crystallisation than the corresponding benzoates, so that in most cases the error from incomplete purification can be reduced to a minimum.

In deciding which acid containing bromine was the best adapted to our purpose, we rejected the fat acids, although, other things being equal, they were to be preferred on account of the greater differences in the percentages of bromine, because we feared the removal of a portion of the bromine in the preparation or purification of the ester, and accordingly selected from the aromatic acids that one which we found could be prepared most easily—that is, the parabrombenzoic acid.

In the remainder of the paper we give the details of the methods which we found most convenient for the preparation of the parabrombenzoic acid and its chloride and anhydride, as well as a few experiments on the formation of parabrombenzoyl esters, undertaken to determine whether these bodies could be formed as easily as the corresponding benzoyl compounds; but we have not considered it necessary to extend these experiments to the less accessible substances, or to multiply them for the commoner bodies, as those which we have tried are sufficient to prove the general application of the method; showing that the parabrombenzoylchloride is as reactive as benzoylchloride, and that the anhydride, although, on account of its high melting-point, somewhat less manageable than the non-substituted one, acts excellently on all substances which can stand a high temperature, and can usually be made to act on those which cannot by heating with anhydrous benzol in a sealed tube. As all the derivatives of parabrombenzoic acid described in this paper, with the exception of the chloride, are new, we give a full account of their properties, as a contribution to our knowledge of this hitherto neglected acid.

Preparation of Parabrombenzoic Acid.

Although this method offers no new features, we think it best to describe it as a matter of convenience for those who may wish to obtain the acid in quantity. The first step is the preparation of crude monobromtoluol by mixing toluol with ten per cent. of its weight of iodine and the calculated amount of bromine. After the mixture has stood at the ordinary temperature for twelve hours, the product is washed with sodic hydrate and water, the bromtoluol fractioned, and the portion boiling from 180° to 190° oxidised by boiling 150 grams of it in a flask with a return-condenser for twelve hours with 400 grams of potassic dichromate and 550 grams of sulphuric acid diluted with twice its bulk of water. The unoxidised oil, consisting of orthobromtoluol with a little para, is distilled off with steam, and the acid purified by washing with water and conversion into the sodic salt. The product is free from the isomeric brombenzoic acids, as shown by its melting-point, 248°–250° (uncorr.). The yield varied from 40 to 70 per cent. of the weight of crude bromtoluol used, and a preparation can be carried through from toluol to the pure acid in less than one week.

Parabrombenzoylchloride, $C_6H_4BrCOCl$.—This substance has been prepared by J. W. Raveill,[1] under the direction of Hübner; but he gives only the most meagre description of it, stating that it forms colorless, easily fusible, volatile needles. It is prepared without difficulty by heating a mixture of phosphoric pentachloride and the dry acid in a flask to 100° until the reaction has ceased, when the temperature is to be raised to 150°, and kept at this point until the greater part of the phosphoric oxychloride formed has passed off. The chloride is then extracted with ligroine and purified by distillation. The yield is about 80 per cent. Its composition was determined by the following analyses:

I. 0.4010 gram of the substance gave on combustion 0.5575 gram of carbonic dioxide and 0.0745 gram of water.

II. 0.2273 gram gave by the method of Carius 0.3448 gram of the mixture of argentic chloride and bromide.

III. 0.4160 gram gave by the same method 0.6278 gram of the mixture of argentic chloride and bromide.

IV. 0.3014 gram gave, when boiled with a solution of pure potassic hydrate, after acidification with nitric acid and precipitation with argentic nitrate, 0.1962 gram of argentic chloride.

[1] Annalen der Chemie **222**, 178, note.

V. 0.4284 gram gave by the same method 0.2773 gram of argentic chloride.

	Calculated for $C_6H_4BrCOCl$.	Found. I.	II.	III.	IV.	V.
Carbon	38.26	37.92	...	...	...	...
Hydrogen	1.82	2.06	...	...	...	...
Chlorine and bromine	52.62	...	52.61	52.86	...	...
Chlorine	16.17	...	...	...	16.08	16.01

Properties.—White needles with an odor similar to that of benzoylchloride, but much less marked, owing to its higher boiling-point; melting-point, 30°. It boils at 245°–247°[1] (uncorr.) with slight decomposition; water does not dissolve it, and acts upon it very slowly, if at all, in the cold, more rapidly when boiling; it is easily soluble in ligroine or benzol, while alcohol dissolves it with conversion into the ethyl ester, a viscous liquid with an odor similar to that of oil of anise.

Parabrombenzoic Anhydride, $(C_6H_4BrCO)_2O$.—This substance was prepared by heating the sodic parabrombenzoate with parabrombenzoylchloride, not in excess; convenient proportions are 3 grams of the sodic salt to 2 grams of the chloride. The mixture was heated in a flask with an air-condenser for an hour to 200° by means of a paraffine bath, and the product purified by washing, first with ligroine, then with a strong solution of sodic carbonate, and finally with benzol to remove the tarry impurities. The yield was about 50 per cent. Owing to its very slight solubility in all the common solvents, we did not attempt to purify it by crystallisation, but this was fortunately unnecessary, as the following analyses show that the substance purified as above by washing is essentially pure:

I. 0.2310 gram of the substance gave by the method of Carius 0.2260 gram of argentic bromide.

II. 0.2167 gram gave 0.2138 gram of argentic bromide.

	Calculated for $(C_6H_4BrCO)_2O$.	Found. I.	II.
Bromine	41.67	41.64	41.99

Properties.—As obtained by the method described above, it forms an odorless, bulky white powder; crystallised from chloroform, it forms minute oblong, rectangular plates; from benzol, small, pointed needles; melting-point, 212°–213°. It is insoluble in water, and

[1] It was not thought worth while to try to determine this temperature with greater accuracy, because of the decomposition with which the boiling is accompanied.

apparently not decomposed by it even when boiling; almost insoluble in ether, glacial acetic acid, or carbonic disulphide; slightly soluble in benzol, somewhat more so in chloroform, which is the best solvent for it; hot alcohol dissolves it freely, converting it into the ethyl ester, as shown by the characteristic odor of that substance. Cold sodic hydrate is essentially without action on it, but decomposes and dissolves it slowly when warmed with it.

Phenylparabrombenzoate, $C_6H_4BrCOOC_6H_5$.—This substance was made by heating phenol and parabrombenzoylchloride in a flask with a return-condenser to about 200°. It was also prepared from phenol and parabrombenzoic anhydride at the same temperature. The product, a waxy solid, was purified by crystallisation from alcohol, dried at 100°, and analysed.

I. 0.1927 gram of the substance gave by the method of Carius 0.1295 gram of argentic bromide.

II. 0.1051 gram gave 0.0710 gram of argentic bromide.

	Calculated for $C_6H_4BrCO_2C_6H_5$.	Found. I.	II.
Bromine	28.88	28.61	28.76

Properties.—White scales with a pearly lustre somewhat resembling naphthaline; it has a slight, agreeable odor, and melts at 117°. It is insoluble in water, readily soluble in alcohol, methyl alcohol, ether, benzol, chloroform, or carbonic disulphide, less so in ligroine, and not freely soluble in glacial acetic acid. Alcohol is the best solvent for it.

Phenylbenzoate is a well-crystallised substance melting at 68°–69°.

Pyrogallol Triparabrombenzoate, $(C_6H_4BrCOO)_3C_6H_3$.—This substance was made by the action of parabrombenzoylchloride on pyrogallol at 100° for six hours. After removing the excess of the chloride with ligroine, the residue was washed with a boiling solution of sodic carbonate, and the slightly yellowish waxy solid purified by crystallisation from hot benzol. Its composition was determined by the following analyses:

I. 0.1569 gram of the substance gave by the method of Carius 0.1322 gram of argentic bromide.

II. 0.1153 gram gave 0.0963 gram of argentic bromide.

	Calculated for $(C_7H_4BrO_2)_3C_6H_3$.	Found. I.	II.
Bromine	35.56	35.85	35.55

Properties.—It forms a white, crystalline powder made up of microscopic, diamond-shaped plates, which belong to the monoclinic

system, to judge from their behavior toward polarised light; melting-point, 140°. Freely soluble in benzol, ether, or chloroform, very slightly soluble in alcohol, glacial acetic acid, or carbonic disulphide, and essentially insoluble in water or ligroine. Hot benzol is the best solvent for it.

It is an important point in favor of our method that this is a crystalline substance, whereas the product of the action of benzoyl-chloride on pyrogallol was, according to Nachbaur,[1] resinous, and the difficulties in the way of its purification were so great that its formula could not be determined with certainty.

Parabrombenzamide, $C_6H_4BrCONH_2$.—This substance was prepared, as a contribution to our knowledge of the derivatives of parabrombenzoic acid, by the action of strong ammonic hydrate on the parabrombenzoylchloride. The white, curdy precipitate thus obtained was purified by three recrystallisations from boiling water. Its composition was determined by the following analyses:

I. 0.3012 gram of the substance gave 18.6 cc. of nitrogen gas under a pressure of 767 mm. and a temperature of 18°.

II. 0.1326 gram of the substance gave by the method of Carius 0.1260 gram of argentic bromide.

	Calculated for $C_6H_4BrCONH_2$.	Found. I.	II.
Nitrogen	7.00	7.20	...
Bromine	40.00	...	40.44

Properties.—It forms small white, rectangular plates with a pearly lustre; melting-point, 186°. It is insoluble, or nearly so, in cold water, soluble in hot, and in alcohol, ether, or glacial acetic acid, very slightly soluble in chloroform, and essentially insoluble in ligroine, benzol, or carbonic disulphide.

ON THE ACTION OF BROMINE ON ISOBUTYLENE.

By L. M. Norton and H. J. Williams.

During the preparation of a large quantity of isobutylene bromide by the absorption of isobutylene in a solution of bromine in carbon disulphide, we observed that the theoretical yield of iso-

[1] Wien. Acad. Ber. **24**, 270.

butylene bromide was not obtained. The isobutylene was prepared by the action of alcoholic soda solution on pure isobutyl iodide,[1] and was then absorbed in a series of bottles containing a mixture of equal volumes of bromine and carbon disulphide. The carbon disulphide and isobutylene bromide were removed by distillation, and a very considerable residue with a high boiling-point remained. By fractionation at a pressure of 235 mm., a liquid boiling at 173°–183° at that pressure was obtained from the residue just mentioned. This liquid possessed a yellow color, and analysis indicated that it was a tribrom-isobutane. Its specific gravity was 2.15 at 17° compared with water at the same temperature. The analysis gave:

	Found.	Calculated for Tribrom-isobutane.
Br	80.95	81.35
H	2.85	2.37
C	17.05	16.27

For further examination the tribrom-isobutane was treated with alcoholic soda solution in the proportion of one mol. of sodium hydrate to one mol. of tribrom-isobutane. The liquid obtained by the action of the soda, after freeing it from alcohol, was purified by fractionation and boiled constantly at 158°–161°. It possessed a yellow color. Two bromine estimations gave 51.59 per cent. and 51.48 per cent. of bromine, while the dibrom-isobutylene, which the treatment described above should have furnished, would contain 74.77 per cent. of bromine. The new compound did not absorb bromine, and was perhaps an isobutylene bromhydrine which would contain 52.28 per cent. of bromine.

It seemed desirable to compare our tribrom-isobutane with a tribrom-isobutane of known structure. For this purpose isocrotyl bromide[2] boiling at 91°–92°, prepared by the action of alcoholic soda solution on isobutylene bromide, was treated with bromine. The tribromide thus obtained was purified by fractionation under reduced pressure, and boiled constantly under a pressure of 235 mm. at 155°–161°. Its specific gravity at 17°, compared with water at the same temperature, was 2.187. An analysis gave:

	Found.	Calculated for Tribrom-isobutane.
Br	80.91	81.36

[1] Chapman and Smith, Jour. Chem. Soc. 7, 153.

[2] Butlerow, Zeit. f. Chem. 1870, 593.

By treatment with alcoholic soda this tribrom-isobutane was converted into a dibrom-isobutylene which boiled constantly at 154°–155°, and is identical with that mentioned by Caventou,[1] and obtained by him from a butylene formed by the action of heat on fusel oil. By the action of bromine this dibrom-isobutylene was converted into a tetrabrom-isobutane which contained:

	Found.	Calculated for Tetrabrom-isobutane.
Br	85.54	85.56

This compound crystallises from ether in beautiful long plates. It is easily soluble in alcohol and ether. It melts with decomposition at 205°, and is without doubt identical with that obtained by Caventou in the above-mentioned research. It appears probable, therefore, that Caventou obtained isobutylene by the action of heat on fusel oil. Isobutylene was obtained in this way by Butlerow,[2] and the butylene of Wurtz,[3] also obtained in the same way and hitherto considered to be pseudobutylene, may perhaps have been isobutylene.

A comparison of the tribrom-isobutane formed by the action of bromine on isobutylene and that formed by the addition of bromine to isocrotyl bromide, leads us to believe that the two tribrom-isobutanes are not identical, since they differ, as the results given above show, in their physical properties and widely in their behavior toward alcoholic soda solution. According to the views ordinarily held, only two tribrom-isobutanes could be formed from isobutylene—viz. $(CH_3)_2 : CBr : CHBr_2$ and $CH_3 : CH_2Br : CBr : CH_2Br$. To the tribrom-isobutane formed from isocrotyl bromide the structure $(CH_3)_2 : CBr : CHBr_2$ must be assigned. There remains only the symbol $CH_3 : CH_2Br : CBr : CH_2Br$ for the tribrom-isobutane formed by the action of bromine on isobutylene. It is probable that the formation of tribrom-isobutane from isobutylene takes place simultaneously with the union of bromine with isobutylene, as we were unable to obtain any tribrom-isobutane by allowing isobutylene bromide to remain in contact with a solution of bromine in carbon disulphide for several weeks.

Massachusetts Institute of Technology, Boston.

[1] Ann. d. Chem. **127**, 96. [2] Ann. d. Chem. **145**, 277.
[3] Ann. d. chim. et phys. [3], **55**, 452.

THE ACTION OF FERRIC SULPHATE ON IRON.

By Albert E. Menke.

The deleterious action of ferric sulphate on boilers has been the cause of much trouble to engineers, owing to the fact that it appears to cause rapid corrosion. Experiments have been made to determine the action of ferric sulphate in solutions of different strengths on different irons, and to see how far it is possible to stop the destructive effects. In the first series of experiments pure iron wire was taken, a certain amount of water and ferric sulphate added, and the whole then heated in flasks with reversed coolers. For purposes of comparison, blank experiments were made with iron and water, leaving out the ferric sulphate. The following results were obtained:

No. of Expt.	Actual Loss.	Calculated on Blank.	Rust Formed.	Amount $Fe(SO_4)_3$ Used.	Weight Fe Taken.
1	.0135	.0133	.0002	.0016	1.1515
2	.0115	.0111	.0004	.0032	.9590
3	.0130	.0112	.0018	.0048	.9660
4	.0193	.0128	.0065	.0064	1.0965
5	.0161	.0108	.0053	.0080	.9314
6	.0214	.0135	.0076	.0096	1.1720
7	.0198	.0122	.0076	.0144	1.0507
8	.0040	.0032	.0008	.0016	.2816
9	.0080	.0033	.0047	.0032	.2805
10	.0050	.0036	.0014	.0048	.3130
11	.0030	.0028	.0002	.0064	.2440
12	.0035	.0026	.0009	.0080	.2295
13	.0036	.0028	.0008	.0096	.2464
14	.0070	.0032	.0038	.0144	.2800
15	.0030	.0030	.0030	None.	.2584
16	.0029	.0029	.0029	None.	.2576

The results in Column 3 were obtained by calculation from Experiments 15 and 16. All were heated the same length of time—fifteen hours. It will be noticed that there is a slight increase of oxidation as the strength of the ferric sulphate increases. The next set of experiments was made with the substances enclosed in sealed tubes and heated to 110° C. for fifteen hours.

No. of Expt.	Amount Rust Formed.	$Fe_2(SO_4)_3$ Used.	Weight Iron Taken.
17	.0005	.0016	.6930
18	.0006	.0016	.7390
19	.0008	.0032	.7860
20	.0005	.0032	.7830
21	.0010	.0048	.8350
22	.0015	.0048	.7700
23	.0002	None.	.7900

It will be noticed here, again, that the rust increases with the ferric sulphate. In the next set of experiments, Nos. 24 and 25 had nothing but the iron and ferric sulphate solution, Nos. 26 and 27 had the calculated amount of sodic carbonate, Nos. 28 and 29 the potassic carbonate, and Nos. 30 and 31 the calcic carbonate requisite for decomposing the ferric sulphate. These experiments were made in sealed tubes heated to 110° C. for fifteen hours. The results are interesting, and show that the alkaline carbonates have a good effect in stopping the formation of rust.

No. of Expt.	Amount Rust Formed.	$Fe_2(SO_4)_3$ Used.	Weight Iron Taken.
24	.0025	.0093	.9596
25	.0028	.0093	.9331
26	.0010	.0093	.9318
27	.0011	.0093	.9166
28	.0010	.0093	.9504
29	.0006	.0093	.9431
30	.0023	.0093	1.0178
31	.0024	.0093	.9666

In the next set of experiments the temperature was raised to 160° C., the tubes being heated, however, only three hours.

No. of Experiment.	Rust Formed.	$Fe_2(SO_4)_3$ Used.	Weight Iron Taken.
32	.0012	.0934	.8898
33	.0004	.0934	.9192
34	.0006	.0934	.9564
35	.0005	.0934	.9340

The action here has been more rapid as the temperature and pressure increased. The next series of experiments was made with boiler-iron of good quality. The pieces of iron used were about one-half inch long, one-eighth inch thick and one-eighth inch wide. The action was not as vigorous as in the experiments with pure iron.

No. of Expt.	Rust Formed.	$Fe_2(SO_4)_3$ Used.	Wt. Iron Taken.	Remarks.
36	.0101	.0934	7.2561	Alone.
37	.0089	.0934	8.6119	Alone.
38	.0045	.0934	9.1265	+ $NaHCO_3$
39	.0035	.0934	8.8775	+ $NaHCO_3$
40	.0040	.0934	9.6142	+ K_2CO_3
41	.0030	.0934	7.9619	+ K_2CO_3
42	.0046	.0934	8.9392	+ $CaCO_3$
43	.0046	.0934	7.5256	+ $CaCO_3$

The above experiments were conducted in sealed tubes heated to 110° C. for 15 hours.

The next set of experiments was made in sealed tubes heated to 160° C. for 3 hours.

No. of Experiment.	Amount Rust Formed.	$Fe_2(SO_4)_3$ Used.	Weight Iron Taken.	Remarks.
44	.0124	.0934	8.2238	Alone.
45	.0052	.0934	6.5678	+ $NaHCO_3$
46	.0048	.0934	6.5075	+ K_2CO_3
47	.0076	.0934	7.3948	+ $CaCO_3$

The action here, as when pure iron was used, has been more rapid. This was proven to be the case by making two experiments and testing the amount of rust formed every hour for ten hours successively. In the tube heated to 110° the action was gradual; in the tube heated to 160° most of the rust was formed in the first hour. How long the action goes on, and at what rate it progresses, has not yet been determined. The next set of experiments was made with small pieces of steel, and here the action was the slowest.

No. of Experiment.	Rust Formed.	Amount $Fe_2(SO_4)_3$ Used.	Wt. of Steel Taken.	Remarks.
48	.0064	.0934	7.7526	Alone.
49	.0062	.0934	7.6843	Alone.
50	.0020	.0934	7.4232	+ K_2CO_3
51	.0025	.0934	7.3965	+ K_2CO_3
52	.0031	.0934	7.5742	+ $NaHCO_3$
53	.0028	.0934	7.4962	+ $NaHCO_3$
54	.0048	.0934	7.7922	+ $CaCO_3$
55	.0042	.0934	7.7800	+ $CaCO_3$

The above were heated to 110° C. in sealed tubes.

The following were heated to 160° C. in sealed tubes:

No. of Expt.	Rust Formed.	Amt. $Fe_2(SO_4)_3$ Used.	Wt. of Steel Taken.	Remarks.
56	.0072	.0934	7.8423	Alone.
57	.0039	.0934	7.6364	+ $NaHCO_3$
58	.0026	.0934	7.7982	+ K_2CO_3
59	.0041	.0934	7.6541	+ $CaCO_3$

Potassium carbonate all through seems to be the best preventive, but its expense will, in most instances, preclude its use. Sodic carbonate was tried in all kinds of proportion, but in no case was there complete arrest of the oxidation. The best amount of sodic carbonate to use is 1½ grains for every grain of ferric sulphate found in the water. Further experiments in the retarding of rust-formation are now in progress.

KENTUCKY STATE COLLEGE.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.

IV.

BY W. A. NOYES AND CHARLES WALKER.

In the last paper[1] it was shown that ortho-toluene sulphamide when oxidised with potassium ferricyanide gives ortho-sulphaminebenzoic acid. As similar substances which have been oxidised by other agents have yielded sulphinides instead of ortho-sulphamine acids, it was of interest to determine whether other ortho sulphamides would conduct themselves in the same way as ortho-toluene sulphamide toward potassium ferricyanide.

The substance chosen for the investigation was para-xylene sulphamide. The para-xylene used was obtained from Kahlbaum. In cold weather it solidified, and the portion which became liquid at 12.5° was drained from the crystals. From the latter the amide was prepared in the usual way. It fused at 147°–148° (uncorr.).

Oxidation of Para-xylene Sulphamide.

The oxidation was effected with somewhat larger quantities than have been used in previous experiments. A mixture of 10 grams

[1] This Journal **8**, 176.

of the amide, 250 grams of potassium ferricyanide, 100 grams of caustic potash and 1000 cc. of water was boiled for about five hours. The oxide of iron which separated was filtered off, the filtrate was cooled, and enough dilute sulphuric acid was added to cause a slight evolution of carbon dioxide. This precipitated most of the unoxidised amide, which was then filtered off and used for a second oxidation, conducted in the same manner as the first. The solutions obtained from the two oxidations were evaporated and the potassium ferrocyanide was mostly removed by crystallisation. The solution was then acidified with sulphuric acid and extracted with ether. The impure acid which remained on distilling the ether was converted into the barium salt, and the solution of the latter was evaporated to dryness and the residue was treated several times with strong alcohol. This dissolved the unoxidised amide which it contained and also, as will be seen further on, a small quantity of a barium salt. The salt which remained was found to consist mainly of *barium sulphamine terephthalate*, which was easily obtained pure by dissolving the salt in a considerable amount of hot water and evaporating the solution till the salt separated.

Sulphamine-terephthalic Acid.

Considerable difficulty was experienced at first in obtaining the free acid in a state of purity, owing to the slight solubility of its barium salt, and to the fact that, when the salt is heated with hydrochloric acid, it is rapidly converted into mono-hydro-barium sulpho-terephthalate. It was shown by a special experiment that by evaporating a few times with hydrochloric acid, the conversion is almost quantitative, the amido group being split off and forming ammonium chloride. The barium salt obtained contained no nitrogen.

0.1385 gram of the salt lost 0.0063 gram H_2O at 260° and gave 0.0811 gram $BaSO_4$, which correspond to 4.55 per cent. H_2O and 34.43 per cent. Ba. Theory requires for $C_6H_3{<}\begin{matrix}CO_2\\SO_3\\CO_2H\end{matrix}{>}Ba + H_2O$, 4.51 per cent. H_2O and 34.34 per cent. Ba. The acid itself is decomposed in a similar way, though less easily, by evaporating with hydrochloric acid.

The acid was finally obtained by adding to the barium salt somewhat more than enough dilute hydrochloric acid to decom-

pose it and extracting with ether in a large test-tube. On distilling the ether and crystallising from hot water, the acid was easily obtained pure. *Sulphamine-terephthalic acid* is difficultly soluble in cold water, ether, or alcohol. It is easily soluble in hot water, and crystallises from the solution, on cooling, in fine needles concentrically grouped. The acid may be heated to 170° without loss in weight. It loses weight slowly at 220°, but no good evidence could be obtained that it was converted into the corresponding sulphinide. The best evidence that it is not converted into the sulphinide, however, lies in the fact that the acid does not fuse at 310° (corr.), while the sulphinide fuses at 297°–299° (corr.). The acid fuses with decomposition over the free flame.

I. 0.1064 gram of the acid gave 0.1033 gram $BaSO_4$ (Keiser).

II. 0.1046 gram of the acid gave 0.1000 gram $BaSO_4$ (Carius).

III. 0.1101 gram of the acid gave 0.00625 gram N.

	Calculated for $C_6H_3\begin{cases}COOH\\SO_2NH_2\\COOH\end{cases}$.	Found.		
		I.	II.	III.
S	13.06	13.32	13.15	...
N	5.71	...	...	5.68

Mono-potassium Sulphamine Terephthalate, $C_6H_3\begin{cases}CO_2K\\SO_2NH_2\\CO_2H\end{cases} + \frac{1}{2}H_2O$. This was prepared by adding to a weighed amount of the acid the calculated amount of a standard solution of potassium carbonate and evaporating the solution slightly. On cooling, the salt separated in needles radiating from centres and forming half-balls on the sides of the beaker. The acid potassium salt of terephthalic sulphinide was prepared, for comparison, exactly as described by Remsen and Hall,[1] and it showed no similar tendency. The salt is difficultly soluble in cold water. It loses nothing in weight at 150°–170°. At 200°–210° it loses weight slowly. At 250°, or a little above, it seems to decompose slightly, as in the first three analyses, in which the salt was heated till the weight was constant at that temperature, the loss was respectively 4.07, 4.18 and 4.28 per cent., which would correspond very closely to two-thirds of a molecule of water. The salt was turned slightly brown in each case, however; and as the salt in the third analysis lost only 3.37 per cent. on the first heating, at

[1] This Journal **2**, 58.

245°, while that of the fourth analysis lost only 2.90 per cent. on heating for three and one-half hours at 240°–245°, it seems probable that the salt really contains only one-half of a molecule of water.

I. 0.1204 gram lost 0.0049 gram H_2O at 250° and gave 0.0352 gram K_2SO_4.

II. 0.1003 gram lost 0.0042 gram H_2O at 250° and gave 0.0296 gram K_2SO_4.

III. 0.1633 gram lost 0.0055 gram H_2O at 245° and gave 0.0479 gram K_2SO_4.

IV. 0.0345 gram lost 0.0010 gram H_2O at 240°–245° and gave 0.01015 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}CO_2K\\SO_2NH_2\\CO_2H\end{cases} + \frac{1}{2}H_2O$.	Found.			
		I.	II.	III.	IV.
$\frac{1}{2}H_2O$	3.08	4.07	4.18	3.37	2.90
K	13.35	13.11	13.23	13.15	13.19

Barium Sulphamine Terephthalate,

$C_6H_3\begin{cases}CO_2\\SO_2NH_2\\CO_2\end{cases}>Ba + H_2O$. When the impure sulphamine-terephthalic acid first obtained by evaporating the ethereal extract is boiled with water and barium carbonate, the barium salt which is formed goes into solution easily and remains dissolved in a comparatively small amount of water. If, however, the salt is once separated from the solution by evaporation, the salt which is deposited becomes very difficultly soluble and requires a large amount of hot water to bring it into solution again. The salt is deposited, on cooling its hot solution, in warty masses without any well-defined crystalline structure. Salts of different preparations, after drying over calcium chloride, lost at 210°–220° amounts of water varying from one to two molecules. The determinations of water given were made with the salt which gave the best evidence of being homogeneous in structure.

I. 0.2859 gram of the salt dried over $CaCl_2$ lost 0.0132 gram H_2O at 220°.

II. 0.3357 gram of the salt dried over $CaCl_2$ lost 0.0157 gram H_2O at 220°.

	Calculated for $C_6H_3\begin{cases}CO_2\\SO_2NH_2\\CO_2\end{cases}>Ba + H_2O$.	Found.	
		I.	II.
H_2O	4.52	4.62	4.68

I. 0.1141 gram of the anhydrous salt gave 0.0703 gram $BaSO_4$.

II. 0.1569 gram of the anhydrous salt gave 0.0961 gram $BaSO_4$.

III. 0.1880 gram of the anhydrous salt gave 0.00693 gram N.

	Calculated for $C_6H_3\begin{cases}CO_2\\SO_2NH_2\\CO_2\end{cases}>Ba$.	Found. I.	II.	III.
N	3.68	...	...	3.68
Ba	36.05	36.23	36.01	...

Terephthalic Sulphinide.

Remsen and Hall,[1] in their study of terephthalic sulphinide, did not prepare the free sulphinide, but only its acid potassium salt. In order to establish more fully the difference between the sulphinide and sulphamine-terephthalic acid, it seemed of interest to prepare the former and also its barium salt. The acid potassium salt of terephthalic sulphinide was prepared exactly as described by Remsen and Hall. In order to prepare the free sulphinide in a similar case, Remsen and Stokes[2] decomposed an acid silver salt with hydrochloric acid. In the present instance it was found simpler to add dilute sulphuric acid (1 : 5 by volume) to the acid potassium salt and extract with ether in a large test-tube. On evaporating the ethereal solution and crystallising the residue from hot water, the sulphinide was easily obtained pure. It crystallises in short, thin prisms. It is moderately soluble in cold, easily in hot water, difficultly soluble in ether. It fuses at 297°–299° (corr.). One of the most characteristic differences between sulphamine-terephthalic acid and terephthalic sulphinide is that solutions of the latter give a precipitate with silver nitrate which is almost insoluble in dilute nitric acid. Sulphamine-terephthalic acid gives no similar precipitate. The analyses were as follows:

I. 0.1040 gram gave 0.1075 gram $BaSO_4$.

II. 0.0849 gram gave 0.0869 gram $BaSO_4$.

III. 0.0547 gram gave 0.00343 gram N.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2>NH.\\CO_2H\end{cases}$	Found. I.	II.	III.
N	6.17	...	...	6.27
S	14.10	14.20	14.05	...

[1] *Loc. cit.* [2] This Journal **6**, 268.

Barium Anhydro-sulphamine Terephthalate,

$C_6H_3—SO_2>N>Ba + 3H_2O$ (CO and CO_2). This was obtained by boiling a solution of the sulphinide with barium carbonate. On evaporating the solution on the water-bath, the salt was deposited in scales which are very difficultly soluble in water.

I. 0.1532 gram lost 0.0197 gram H_2O at 250° and gave 0.0860 gram $BaSO_4$.

II. 0.1875 gram lost 0.0241 gram H_2O at 250° and gave 0.1048 gram $BaSO_4$.

	Calculated for $C_6H_3—SO_2>N>Ba + 3H_2O$.	Found. I.	Found. II.
$3H_2O$	12.98	12.86	12.85
Ba	32.93	33.00	32.86

Formation of Sulphamine-para-toluic Acids.

While sulphamine-terephthalic acid is formed in larger quantity than anything else when para-xylene sulphamide is oxidised by means of potassium ferricyanide, it is not the only product of the oxidation. In recrystallising the barium salt which had been purified by treatment with alcohol, after removing most of the barium sulphamine terephthalate there remained in solution a much more soluble barium salt. Dilute hydrochloric acid precipitated an acid from this solution which, after several crystallisations from water, proved to be the same sulphamine-para-toluic acid which was obtained by Remsen and Hall[1] by oxidising para-xylene sulphamide with chromic acid. These authors state that the acid is insoluble in ether, while we obtained it from the ethereal extract, and found that it was in reality slightly soluble in ether. In other respects the acid obtained by us as described above agreed in properties with those ascribed to sulphamine-para-toluic acid. It fused at 267° (uncorr.). Fused with caustic potash in the manner described by Remsen and Hall,[2] it yielded oxy-toluic acid, C_6H_3(COOH 1, OH 3, CH_3 4), which fused at 206°–208°, and oxy-terephthalic acid which did not fuse at 300°. The acid was also analysed: 0.0981 gram gave 0.1064 gram $BaSO_4$, which corresponds to 14.89 per cent. of S. Theory requires 14.79 per cent.

[1] This Journal **2**, 50. [2] This Journal **2**, 54.

In the first part of this paper it was stated that the alcoholic solution obtained in the purification of the barium salts also contained a small quantity of a barium salt. The solution was evaporated to dryness and the residue was dissolved in a little hot water. On cooling the solution, most of the para-xylene sulphamide which it contained separated. This was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in hot alcohol, in which it was quite easily soluble. After cooling, an equal volume of ether was added. This caused the precipitation of the barium salt. After filtering, the residue was treated again in the same way, to remove the last traces of the para-xylene sulphamide. An attempt to crystallise the barium salt from water being unsuccessful, the aqueous solution was precipitated with hydrochloric acid. The acid separated as an oily liquid at first, but it soon solidified. Repeated crystallisation from hot water failed to give any pure substance from this. Different specimens fused at temperatures ranging from 190°–240°. The portion most easily soluble in hot water, which melted partially at 192°–193°, was fused with caustic potash. The fusion was dissolved in water and the solution was acidified with hydrochloric acid. On distilling the solution the distillate deposited a small amount of an acid which fused at 173°–174° (corr.), and whose solution gave a strong violet color with ferric chloride. This was evidently nearly pure β-oxy-para-toluic acid, $C_6H_3\begin{cases}\text{COOH} & 1.\\ \text{OH} & 2.\\ \text{CH}_3 & 4.\end{cases}$ It must have come either from para-toluic sulphinide or from a β-sulphamine-para-toluic acid containing the sulphamine group ortho to the carboxyl. The latter supposition seems the more probable.

The formation of a second sulphamine-para-toluic acid is of especial interest, as it shows that in this case, where there are two methyl groups to be oxidised, they are attacked with about equal ease by potassium ferricyanide, although one group is ortho and the other is meta to the sulphamine group.

UNIVERSITY OF TENNESSEE, *July* 16, 1886.

Contributions from the Laboratory of the Wisconsin Agricultural Experiment Station.

ANALYSIS OF MILK.

By F. G. Short.

In carrying on a series of feeding experiments at this station, it was found necessary to shorten and simplify as much as possible the method of milk analysis. The experience of four years and the analysis of over one thousand samples of milk have shown that the following method is entirely satisfactory when the number of samples is large and time and labor are important considerations.

The following apparatus is required:

Hofmeister capsules of very thin glass, of a capacity of 10–15 cc. Asbestos, of the long, silky variety, prepared by heating to redness for one hour and kept in a glass-stoppered bottle. A five cc. pipette graduated in tenths. Some form of continuous fat extractor. Flasks holding about 100 cc. Dry ether, prepared by allowing commercial stronger ether to stand over fused calcium chloride for several days, with occasional shaking, and then distilling off. Cheese-cloth that has been prepared by being extracted with dry ether.

The milk is thoroughly mixed by pouring several times from one vessel to another. A Hofmeister capsule about three-fourths filled with the prepared asbestos is placed on the balance pan, covered with a small beaker, and weighed. A small beaker weighing about twelve grams is kept in the balance for this purpose.

Two cubic centimetres of milk are allowed to run into the capsule from the five cc. pipette; the capsule is immediately transferred to the balance, covered with the beaker, and a second weight taken. In a rich milk, such as was given by the Jersey cows used in the experiments, it is impossible to measure the milk with sufficient accuracy by means of a pipette. If the sample is thoroughly mixed, two grams will be found sufficient for accurate work. Enough asbestos must be used to entirely absorb the milk, thus presenting a large surface for evaporation.

The capsules and contents are dried at 110° C. in a double-walled oven containing a solution of chloride of calcium boiling

at 110° C. To the oven is attached an upright condenser, to return the steam from the boiling calcium chloride solution. The chloride of calcium bath is found preferable to an oven heated directly by gas, on account of the ease with which a constant temperature is maintained. The oven in the station laboratory has been in use for several months, and has not varied a degree centigrade in that time. The only precaution is that the solution must boil freely at 110° C. The capsules containing milk are allowed to remain in the oven two hours. For the first twenty minutes the door of the oven is left partly open, to allow the excess of water to pass off. The door is then closed, and a slow current of dry carbonic acid gas is passed through the oven. At the end of two hours the capsules are removed to a desiccator, cooled and weighed.

For the fat, an extractor of the form given by S. W. Johnson is used.[1] The capsule is wrapped in a piece of prepared cheese-cloth, crushed between the fingers and slipped into the inside tube. The cloth should be packed tight, so that during the extraction the column of ether will nearly fill the inside tube. A dry, weighed flask is attached to the extractor, fifty cc. of dry ether are poured in, and the whole connected to an upright condenser. In the station laboratory twelve condensers are used, fixed in a wooden frame. The water enters at one side and passes successively through each condenser. The flasks dip into a copper tank, four inches square and two feet five inches long, containing water heated by a Bunsen burner. The apparatus, once adjusted, requires no further attention. At the end of two hours the flasks are removed and the ether distilled off. The flasks are then wiped dry and placed in the drying-oven, where they are heated three hours in an atmosphere of carbonic acid gas, cooled and weighed. A series of analyses of the same milk gave the following:

Solids.	Fat.
13.71	3.75
13.41	3.72
13.48	3.73
13.46	3.77
13.53	3.89
13.48	3.90
13.19	3.75

[1] American Journal of Science, June, 1877.

13.30	3.73
13.20	3.78
13.26	3.82
13.43	...
Average, 13.35	3.78 Average.
Highest, 13.71	3.72 Lowest.
Lowest, 13.19	3.90 Highest.

A comparison of the above method with that of Adams[1] gave the following:

	Fat by Adams's Method.	Fat by Station Method.
1	5.89	5.94
2	5.91	5.84
3	5.92	5.83
Average,	5.89	5.87

The above method is also applicable to butter analysis. The sample of butter is prepared by the method given by S. M. Babcock.[2] The sample, of one-half to one pound, is placed in a wide-mouthed fruit jar, the cover screwed down, and the butter melted by immersing the jar in warm water. As soon as the sample is thoroughly melted, the jar is shaken vigorously until a perfect emulsion of water and fat is secured.

The shaking is continued until the butter is so nearly solid that no separation of water and fat can take place. To hasten the cooling the bottle is held under the water-faucet. A small (*oo*) porcelain dish is taken, two to four grams of prepared asbestos placed in it, and the whole weighed. Between two and three grams of butter are placed on the asbestos, and dish and contents weighed again. If enough asbestos is taken, the butter is all absorbed when heated, and no difficulty is found in transferring the dried fat to the extractor.

The butter is dried two hours at 110° C. in an atmosphere of carbonic acid gas, cooled and weighed. The dry fat is transferred to the extractor by means of a piece of cheese-cloth, and the dish washed out with a few drops of ether. Fifty cc. of ether are added and the extraction continued for one hour, as for milk.

A series of determinations on the same sample of butter gave:

[1] Analyst **10**, 50. [2] N. Y. Agl. Station Report, 1886, 334.

Water.	Fat.
12.70	83.62
12.57	83.49
12.63	83.62
12.72	83.46
12.64	83.21
12.72	83.57
12.73	82.96
12.64	83.43
12.72	83.29
12.68	83.31
12.61	83.33
Average, 12.67	83.55 Average.
Highest, 12.73	83.62 Highest.
Lowest, 12.57	82.96 Lowest.

AGRICULTURAL EXPERIMENT STATION, MADISON, WIS., *March* 23, 1887.

ON THE COMPOSITION OF POTATOES.

BY M. A. SCOVELL, DIRECTOR, AND ALBERT E. MENKE, OF THE KY. AGR. EXP. STATION.

The percentage of starch in potatoes has been considered to be in direct ratio with their specific gravity. There are several tables in existence; one by Heideprinn,[1] another by Marke,[2] have usually been adopted for their accuracy. We have made a great many determinations of starch in potatoes, and do not find that the tables agree with our results to a striking degree; nor, on the other hand, do the tables agree with each other: they have apparently been mostly calculated from a few determinations. We show in the table appended the discrepancies between our results and those heretofore accepted. The starch was determined by acting upon the dried and finely pulverised potato with sulphuric acid, and heating in closed bottles at a temperature of 110° C. for four hours, in order to insure conversion, and then titrating in the usual way

[1] Landw. Versuch-station **20**, 17. [2] Dingl. Polyt. Jour. **225**, 517.

with Fehling solution. In order to correct any error that might ensue from the presence of sugar in the potato prior to the above treatment, we squeezed out the juice from a corresponding sample of undried potato, boiled it with acid as before, neutralised with potash, decolorised with subacetate of lead, filtered, diluted, and titrated with Fehling solution. This gave us the amount of sugar and convertible substances present, which could then be deducted by simple calculation from the amount found in the dried potato, giving us the actual sugar due to starch. Our experiments were made on various kinds of potatoes, with the following results:

VARIETY.	Specific Gravity	Dry Substance, Per Cent.	Per Cent. Dry Substance from Specific Gravity	Starch Per Cent.	Per Cent. Starch by Specific Gravity.	Per Cent. Sugar, Gum, etc., calculated as Glucose.	Specific Gravity of Juice.
Empire State	1.0902	22.40	23.98	15.48	16.35	0.88	1.0260
Early Rose, A	1.0902	22.08	23.98	15.15	16.35	0.99	1.0285
" B	1.0895	22.25	23.98	15.18	16.35	1.06	1.0275
" C	1.0861	21.72	23.02	14.57	15.42	0.97	1.0265
Triumph	1.0852	21.80	22.78	15.09	15.19	0.76	1.0245
Burbank, Castle	1.0923	21.46	24.46	14.98	16.81	0.74	1.0255
Beauty of Hebron	1.0849	21.29	22.78	14.56	15.19	0.94	1.0260
Early Ohio	1.0828	21.10	22.30	14.35	14.73	0.77	1.0270
Jumbo	1.0780	20.43	21.13	14.20	13.58	0.84	1.0245
Charter Oak	1.0879	22.91	23.50	15.33	15.88	1.49	1.0310
Clark's No. 1	1.0919	22.35	23.98	15.29	16.35	1.06	1.0275
Perfect Peachblow	1.0843	22.22	22.54	15.12	14.96	1.32	1.0290
Pearl of Savoy	1.0867	21.86	23.26	15.07	15.65	1.06	1.0275
St. Patrick	1.0801	20.20	21.60	14.29	14.04	0.74	1.0240
White Star	1.0878	21.82	23.50	15.11	15.88	0.81	1.0270
Shaker Russet	1.0731	20.42	19.95	13.91	12.44	0.84	1.0280
Dakota Red	1.0733	19 21	19.95	12.05	12.45	1.10	1.0280
Vanguard	1.0828	21.03	22.37	14.76	14.73	0.87	1.0255
Burbank, B. D. P	1.0890	21.94	23.74	16.05	16.12	...	...
Burbank, A. & M	1.0790	20.45	21.37	14.59	13.81	...	...

We have endeavored to found a table on our results, but find that varying conditions affect the percentage of starch in so marked a degree, without producing a corresponding variation in the specific gravity, that we cannot draw up any rigorous table. An approximation to the per cent. of starch present is the best that can be said of specific-gravity indications when different varieties of potatoes are used. The per cent. of sugar in the potato is also at considerable divergence from what might have been expected from a mere specific-gravity determination.

In order to try the effect of various fertilisers on the per cent. of starch present, we made a series of experiments with Burbank potatoes. The per cent. of sugar seemed to keep in fairly constant ratio with the starch, but, as before, the specific gravity did not show the per cent. of starch. The experiments are tabulated below. One-tenth of an acre of ground was used in each experiment.

Variety.	Specific Gravity.	Dry Substance, Per Cent.	Dry Substance, Per Cent. from Sp. Gr.	Starch, Per Cent.	Starch, Per Cent. by Specific Gravity.	Per Cent. Sugar, Gum, etc., calculated as Glucose.	Specific Gravity of Juice.	Fertilisers.
Burbank.	1.0877	22.49	23.50	15.44	15.88	1.03	1.0260	None; potatoes small.
"	1.0843	21.31	22.54	15.34	14.96	0.63	1.0240	None; potatoes cut to 1 eye.
"	1.0741	20.60	20.18	14.80	12.67	0.76	1.0240	None; potatoes large, whole.
"	1.0827	21.50	22.30	15.28	14.73	0.68	1.0235	$NaNO_3$, 30 lbs.; K_2SO_4, 20 lbs.; Superphos., 60 lbs.
"	1.0748	21.04	20.41	15.20	12.89	0.75	1.0255	Superphos., 60 lbs.; $NaNO_3$, 30 lbs.; KCl, 20 lbs.
"	1.0794	21.75	21.36	15.97	13.81	0.95	1.0270	Superphos., 60 lbs.; K_2SO_4, 20 lbs.
"	1.0868	21.60	23.26	15.13	15.65	0.65	1.0240	Superphos., 60 lbs.; $NaNO_3$, 30 lbs.
"	1.0877	22.38	23.50	15.80	15.88	0.93	1.0260	$NaNO_3$, 30 lbs.; K_2SO_4, 20 lbs.
"	1.0882	22.15	23.50	15.56	15.88	0.74	1.0261	Mapes' fertiliser.
"	1.0918	22.74	24.46	15.98	16.81	0.88	1.0275	Blank.
"	1.0837	21.33	22.54	14.65	14.96	0.88	1.0275	Stable manure, 300 lbs.
"	1.0898	21.58	23.74	14.69	16.27	0.92	1.0270	Pulverised limestone, 100 lbs.
"	1.0880	21.85	23.50	15.43	15.88	0.96	1.0280	Homestead fertiliser, 60 lbs.

The nitrogenous constituents of potatoes are at present but partially investigated. They are with difficulty separable, and easily decomposed. We have made extractions by diffusion, and determined the amount of albuminoids in each successive extract. It would appear that a dilute solution of hydrochloric acid will extract seventy-five per cent. of the albuminoids present in potatoes. Three ounces of potatoes were cut up in very thin slices, and successively treated with water, dilute sodium chloride solution, dilute hydrochloric acid, boiling alcohol, dilute hydrochloric acid at 60° C., and cold dilute sodium carbonate. The thin slices were treated with water at the ordinary temperature for two days. The extract was brownish-red in color, and had a distinctive odor. This extract was now boiled down considerably,

when a coagulum separated out. The coagulum was filtered off, and the filtrate evaporated to dryness in a dish which contained sand; otherwise it was impossible to remove the residue from the dish. This process was adopted for each extract, and the albuminoids present were determined by burning with slaked lime. The odd numbers are the coagulums, and the even numbers the filtrates.

Number.	Per Cent. Albuminoids.	How Obtained.
1	.049625	H_2O, 2 days.
2	.047500	
3	.0033500	H_2O, 2 days.
4	.0312500	
5	.008700	.1 per cent. NaCl, 2 days.
6	.017500	
7	.039370	.1 per cent. HCl, 3 hours.
8	.103120	
9	.030620	.1 per cent. HCl, 2 days.
10	.455687	
11	.017500	C_2H_5OH, 5 hours.
12	.153120	
13	.019790	.1 per cent. HCl at 60° C., 6 hours.
14	.250937	
16	.050310	.2 per cent. Na_2CO_3, 2 days.
18	.313656	Residue dried and burnt.

The peptones present in Early Rose, Burbank, Charter Oak and Dakota Red potatoes were determined as follows: The potatoes were mashed in a crusher, the juice obtained was filtered, the filtrate acidified with acetic acid and boiled; the coagulum resulting was then filtered out. The filtrate was now partially decolorised with subacetate of lead, taking care to avoid any excess, the precipitate was filtered off and sulphuretted hydrogen passed through the solution to get rid of any excess of lead, again filtered, acidified with sulphuric acid, and phospho-tungstic acid was added to precipitate the peptones. The precipitate, after washing with acidulated water, was decomposed by baryta water; the yellowish filtrate containing the peptones was treated with carbonic anhydride, which precipitated the rest of the coloring-matter along with the barium carbonate. The quantity of peptone in solution was now estimated by making use of the biuret reaction and a standard solution of fibrin peptone. Again the peptones were precipitated by tannic acid, after precipitation of the albumen

by acetate of lead. The quantity of peptone obtained in this way differed from the amount obtained in the prior method. This was evidently to be accounted for by the fact that phospho-tungstic acid precipitates other matters besides peptones. In order to obtain the amount of peptones as accurately as possible, it is advisable to precipitate them fractionally. The first flocculent precipitate obtained contains all the peptones; the latter pulverulent precipitate contains none.

Variety.	Peptones.	Total Albuminoids.
Early Rose,	.0380 per cent.	2.19 per cent.
Burbank,	.0312	2.25
Charter Oak,	.0294	2.69
Dakota Red,	.0418	2.44

We expected that the Dakota Red potato would yield a much larger percentage of peptones than any other variety, owing to the large amount of solid matter other than starch contained in this potato. The excess of its peptone percentage is, however, but small.

The leucine and tyrosine were determined in the alcoholic extract of the dried potatoes and separated by fractional crystallisation. On concentration crystalline tufts of tyrosine were first deposited, and from the mother liquors, on further concentration, scales of leucine separated. The leucine melts at 170° C., and may be sublimed unchanged, is fairly soluble in water and but slightly so in absolute alcohol. The crude crystals of tyrosine may be purified by solution in hydrochloric acid and precipitation with sodium acetate, digestion with animal charcoal, if necessary, being previously resorted to with the acid solution. It forms long, silky crystals, very sparingly soluble in cold water and alcohol. We found the following amounts present in four varieties:

Early Rose,	.0074
Burbank,	.0068
Dakota Red,	.0092
Charter Oak,	.0070

Asparagin may be separated by adding alcohol to the potato juice and purifying the precipitate. We did not make any determinations of the amount present.

Lexington, Ky.

A METHOD FOR THE DETERMINATION OF BUTTER IN MILK.

By H. N. Morse and C. Piggot.

Briefly stated, the method of which we here give a preliminary account consists in the dehydration of the milk by means of anhydrous sulphate of copper; the extraction of the fat by means of the low-boiling products of petroleum; the saponification of the butter by means of an excess of a standard solution of potassium hydroxide in alcohol; and the determination of the excess of the alkali by means of a standard solution of hydrochloric acid.

The required apparatus and materials are:

1. A porcelain mortar, with lip, having an internal diameter of 85 or 90 millimetres.

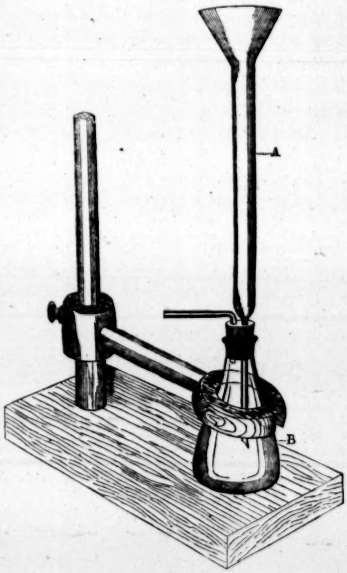
2. An extraction tube, *A* in the figure, having an internal diameter of 14 or 15 millimetres, a length of 220 millimetres and a funnel end 75 millimetres wide. The small end should be beveled. If such a tube is not at hand, a straight chloride of calcium tube of like dimensions and a copper funnel such as is usually employed in filling combustion tubes will suffice. The narrow portion of the tube is filled with cleansed cotton wool, which should be compact enough to prevent the passage of solid matter, and yet not so tightly packed as seriously to impede the filtration of the fat solution. One soon learns, by simply drawing air through the tube with the mouth, to judge correctly whether the filter will satisfy these conditions.

3. A 200 cc. Erlenmeyer flask, *B* in the figure, the strength of which should be tested by the filter pump before using.

4. A suitable stand to hold the flask and extraction tube in position. The figure represents a very convenient form for the purpose. A filter pump which will raise a column of mercury to a height of 26 inches suffices for the operation of five such apparatuses at the same time; hence, for the sake of compactness and convenience, we employ them in series of five each, the bases being fastened together by screwing them down to a board placed underneath. A half-inch brass tube with a small side tube for each flask is fastened to the base between the flasks and the standards. Each side tube is attached to its flask by means of a

short piece of rubber tubing, and supplied with a Mohr's pinch-cock. One end of the larger tube is closed by a stopper, and the other attached to the filter pump.

5. A supply of 10 cc. full pipettes with but one mark. These should be tested, and only those selected which deliver very nearly the normal amount of water. If care is taken to use a clean pipette for each measurement, and to blow out all of the milk which can be removed from it, it is not necessary in ordinary work to weigh, since the difference between the weight of the milk calculated from the volume and the specific gravity, and that found by actual weighing, will only slightly affect the estimated percentage of butter in the second decimal place. We have convinced ourselves by repeated experiments that such wide differences between the estimated and determined weights of milk as are sometimes recorded are not necessary.



6. A number of small weighing glasses, with ground-glass stoppers, to be used when great accuracy in the determination of the butter is required. These should be numbered, and the number of each written upon both the glass and its stopper.

7. A low-boiling "gasoline." This we are accustomed to prepare from the crude product known as "90° gasoline" by agitating it successively with strong sulphuric acid and sodium hydroxide and then distilling. Thus far we have employed only that portion

which distils over between 30° and 60°, though during the summer months it would probably be advisable to reject all of that which comes over below 40° or 45°.

8. Thoroughly dehydrated sulphate of copper.

9. A one-half normal solution of potassium hydroxide in 95 per cent. redistilled alcohol.

10. A one-half normal solution of hydrochloric acid.

The method of procedure in making the determination is as follows: About 20 grams of the copper sulphate are measured off by means of a copper scoop made to hold that amount, and placed upon the bottom of the porcelain mortar. The surface is then somewhat depressed in the centre by the pestle. Ten cc. of milk, measured, or measured and weighed if great accuracy is required, are spread over the sulphate in such a way that none of it can come in contact with the porcelain. When the drying of the milk, which requires only a few minutes, is seen to be nearly complete, the mass is ground up, with the addition of a little clean sand, and transferred to the extraction tube. During the filling of the tube the side of it should occasionally be tapped, in order to render the mass compact. The Erlenmeyer flask is attached to the pump, and the mortar washed with three portions of the benzene, of from 10 to 15 cc. each, care being taken to allow each portion to filter through completely before another is added. Nine other portions of from 10 to 15 cc. of benzene are now poured into and drawn through the tube, the same precaution as to the complete filtration of each portion before the addition of another being observed. It is not certain that so large a number of extractions is necessary, but we have repeatedly assured ourselves that twelve such washings are sufficient to remove every trace of butter from the tube.

The flask is removed to the water-bath and the volume of the butter solution reduced by evaporation to 10 cc. or less, when 20 cc. of the one-half normal solution of caustic potassa are added. The flask is now returned to the water-bath and heated for fifteen minutes. Finally, the excess of alkali is determined by means of the one-half normal solution of hydrochloric acid, with use of phenolphthalein as the indicator. We do not attempt to keep the alcoholic solution of alkali up to standard, but determine each day the number of cubic centimetres of it required to exactly neutralise twenty cubic centimetres of the acid solution, and add that volume to the flask for each saponification.

According to Koettstorfer,[1] the average amount of potassium hydroxide required to saponify one gram of butter is 227 milligrams; but the results of several experiments to determine the amount required to saponify the butter which had been extracted from the dried residue of milk and estimated by the usual gravimetric method, indicate that the number 230 is more correct. Hence that number has been employed in the calculation of the results here given.

Having found the volume of alkali solution required for the saponification, the quantity of butter which it represents is determined by multiplying by 28 (the number of milligrams of KOH in 1 cc. of the solution) and dividing by 230 (the number of milligrams required to saponify 1 gram of butter).

The following table gives a comparative statement, in percentages, of the results obtained by the analysis of five different specimens of milk. The quantity of milk was determined in every case by weighing. The first column, *a*, gives the percentages obtained by the usual gravimetric method of determining butter in milk; the second, *b*, those obtained by saponification of the butter thus determined; while the third, *c*, exhibits the results obtained by the method just described.

a.	*b.*	*c.*
	I.	
5.45 per cent.	5.40 per cent.	5.42 per cent.
	II.	
2.53 per cent.	2.57 per cent.	2.59 per cent.
...	...	2.61
	III.	
4.59 per cent.	4.71 per cent.	4.70 per cent.
...	...	4.58
	IV.	
4.13 per cent.	4.15 per cent.	4.28 per cent.
4.15	4.17	4.29
	V.	
3.75 per cent.	3.84 per cent.	3.84 per cent.
3.81	3.78	3.88

The agreement between the results obtained by the gravimetric method and those by the method here described is, at least, satis-

[1] Zeitschrift für analyt. Chemie **18**, 199 and 431.

factory. The expeditiousness and simplicity of the method also recommend it.

A series of ten determinations was undertaken by Mr. W. M. Burton, of this laboratory, to whom we are much indebted for assistance in working out the method, in order to ascertain how many estimations a single analyst could be expected to complete within a given time. They were completed in less than four hours, with the following percentage results:

3.28, 3.21, 3.32, 3.25, 3.21, 3.25, 3.28, 3.28, 3.25, (3.36). The last result was vitiated by the presence of a small quantity of copper sulphate in the flask which had found its way through the cotton filter.

The collection of apparatus which we would recommend for the rapid execution of a large number of analyses consists of two such series of stands (of five each) as we have already described, ten flasks and extraction tubes, ten pipettes, not less than five mortars, two filter pumps, and a water-bath with holes enough to accommodate eight or ten flasks. With such conveniences and the requisite materials at hand, one analyst could easily complete from twenty-five to thirty determinations within a day of eight hours.

The method is still under examination with reference to the improvement of its details. The most advantageous change which, if it is practicable, could be made, relates to the concentration of the standard solutions. It is to be hoped that $\frac{1}{10}$ or $\frac{2}{10}$ normal solutions may be substituted for the $\frac{1}{2}$ normal ones now in use, and the exactness of the method thereby correspondingly increased.

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ON THE ADDITION OF SODIUM ACETACETIC ETHER AND ANALOGOUS SODIUM COMPOUNDS TO UNSATURATED ORGANIC ETHERS.

BY ARTHUR MICHAEL.

I.

In the synthesis of carbon derivatives, the methods generally in use start from saturated compounds, and the linking of carbon to

carbon takes place by substitution, addition, condensation, or polymerisation. The conversion of unsaturated compounds into saturated of a higher carbon series has been realised in several instances; but, especially in the fatty series, these are few in number, and have not led to a general method. Claus[1] has shown that allyl iodide, potassium cyanide and alcohol heated in a sealed tube give the nitrile of pyrotartaric acid, and believes that when α-chlorcrotonic acid is used, instead of allyl iodide, tricarballylic acid is formed.[2] He did not, however, succeed, in generalising the reaction.

We are indebted to Balsohn[3] for the interesting discovery that ethylene unites with benzene in the presence of aluminium chloride to form mono-, di- and triethylbenzene. Silva[4] has shown that allyl chloride, acting on the benzene-aluminium chloride mixture, gives diphenylpropane, and Essner[5] that amylene unites with benzene under the same conditions to form dimethyl-ethyl-phenyl-methane. This reaction was used by Demole[6] in an attempt to determine the constitution of α-dibromethylene, and Angelbis and Anschütz[7] have proved that when vinyl bromide instead of ethylene is used, a mixture of diphenylethane and dimethyl-anthracene-hydride is obtained. It is not unlikely that the Balsohn method is capable of further generalisation for the synthesis of aromatic hydrocarbons.

I shall describe in this paper a synthetical method of building up carbon derivatives by the direct union of carbon and sodium to unsaturated carbon atoms. This method is based on the property of unsaturated organic ethers of adding directly to sodium derivatives of organic compounds that contain the metal in direct union with carbon. In this reaction the metal unites with an unsaturated carbon, and the negative organic radical with the adjacent unsaturated carbon. It will be noticed that the reaction bears a strong analogy to the formation of halogen derivatives by the union of halhydric acids to unsaturated compounds, as in both reactions we have unsaturated compounds splitting up reagents into positive

[1] Annalen der Chemie **191**, 37. [2] Berichte d. deutsch. chem. Gesell. **14**, 1084.
[3] Bull. Soc. Chim. **31**, 540. [4] *Ibid.* **36**, 66. [5] *Ibid.* **36**, 212.
[6] Demole considered that there is a direct substitution of bromine by phenyl, and therefore that the formation of unsymmetrical diphenylethylene in the reaction proved the constitution of α-dibromethylene. In a discussion of his work I showed that this interpretation is improbable, and that the first stage of the reaction probably consisted in an addition to form styrene-dibromide. (This Journal **5**, 193.)
[7] Berichte d. deutsch. chem. Gesell. **19**, 167.

and negative components to unite with them, forming saturated substances. I have endeavored, in the experiments described below, to select a few typical instances, in order to show the range and capability of the reaction.

Action of Sodium Malonic Ether on Ethyl Cinnamate.

The substances were used in molecular proportions: 4.6 grams sodium were dissolved in 50 grams absolute alcohol, and 32 grams malonic ether added to the solution. On adding the required amount of cinnamic ether (34 grams), it was noticed that the precipitate of sodium malonic ether soon went into solution that became slightly yellow. This solution was heated in a sealed tube in a water-bath for six hours, and then in an open vessel at 100° until the greater part of the alcohol was expelled. The residue was then mixed with water, acidified, extracted with ether, and the extract, after drying over calcium chloride, fractionated under ordinary pressure. It was found that very little unchanged malonic or cinnamic ether remained, and that the main product of the reaction went over between 305° and 310° under slight decomposition. The decomposition may be prevented by fractionating in a vacuum, when, under a pressure of 15 mm., it is easy to isolate a colorless, heavy oil boiling at 213°–215° (oil-bath, at 260° thermometer to 40° in vapor).

An analysis gave the following results:

0.2705 gram substance gave 0.6403 gram CO_2 and 0.1785 gram H_2O.

	Calculated for $C_{18}H_{24}O_6$.	Found.
C	64.29	64.55
H	7.10	7.32

The substance $C_{18}H_{24}O_6$ is formed by the direct union of cinnamic ether to sodium malonic ether, and replacement of sodium by hydrogen. These reactions are represented by the following equations:

$$C_6H_5-CH-CH-COOC_2H_5 + NaHC-(COOC_2H_5)_2 =$$
$$C_6H_5-CH-CHNa-COOC_2H_5$$
$$\quad\quad\quad

$$C_6H_5-CH-CH_2-COOC_2H_5$$
$$\quad\quad|$$
$$\quad CH-(COOC_2H_5)_2 \quad + NaOH.^1$$

It was subsequently found that the reaction proceeds in the cold, and that even better results are thus obtained than by heating. A flask containing an alcoholic solution of cinnamic ether and sodium malonic ether was allowed to stand at ordinary temperature for five days, the contents of the flask then thrown into about five times its volume of water and extracted with ether. After evaporating the ether on a water-bath the residue was fractionated in a vacuum and was found to consist almost entirely of the new ether. To obtain the corresponding acid the ether was saponified with alkali. A mixture of 15 grams of the ether, 16 of caustic potash and 20 of water was heated on a water-bath, but no decomposition was noticed after heating an hour. It was then heated to boiling for about ten minutes, when the ether disappeared. The solution was acidified and extracted with ether, when, after evaporation of the solvent, an oily substance remained. This substance was probably an acid ether, notwithstanding the fact that a considerable excess of alkali was used. It was treated with a solution of 10 grams of caustic potash in an equal amount of water, when a violent reaction took place with the evolution of alcohol. To make sure that the saponification was complete the solution was kept at boiling for two hours. It was found more advantageous, however, to decompose the ether with barium hydrate. Eight grams of the ether were heated for several hours to boiling with a solution of 24 grams of the hydrate in 60 grams of water. The ether gradually disappeared, to make place for a white precipitate of the barium salt. This was dissolved in dilute hydrochloric acid, the barium removed by addition of sulphuric acid and filtration, and the filtrate extracted with ether. The heavy, oily substance that remained after the ether was driven off did not solidify, but when heated for a long time at 100° C. a constant but slow evolution of carbon dioxide took place, and the oil gradually became solid. This may be effected in a much shorter time by heating the oil to 110°–120°. The crystalline residue was purified by several crystal-

[1] In these equations it is assumed that the negative part of the additive compound takes the β-position towards the carboxyl—a supposition that is extremely probable. I shall endeavor, however, to furnish positive proof of the correctness of this view. The compound is the ether of β-phenyl γ-dicarboxyl-butyric acid.

lisations from a *small quantity of alcohol.* It gave on analysis the figures appended:

0.2529 gram substance gave 0.5686 gram CO_2 and 0.1350 gram H_2O.

0.2372 gram substance gave 0.5550 gram CO_2.

	Theory for $C_{11}H_{12}O_4$.	Found.	
C	63.81	64.19	63.77
H	5.76	5.99	

The acid crystallises in needles that are difficultly soluble in water, quite soluble in hot, moderately in cold alcohol. It melts at 137.5°–138.5° and has the constitution of a phenylglutaric acid, as is shown by the following equations:

$$\begin{array}{l} C_6H_5-CH-CH_2-COOC_2H_5 \\ \quad\quad\quad | \\ \quad\quad CH-(COOC_2H_5)_2 \end{array} + 3KOH = \begin{array}{l} C_6H_5-CH-CH_2-COOK \\ \quad\quad\quad | \\ \quad\quad CH-(COOK)_2 \end{array} + 3C_2H_6OH;$$

$$\begin{array}{l} C_6H_5-CH-CH_2-COOH \\ \quad\quad\quad | \\ \quad\quad CH-(COOH)_2 \end{array} = \begin{array}{l} C_6H_5-CH-CH_2-COOH \\ \quad\quad\quad | \\ \quad\quad CH_2-COOH. \end{array} + CO_2$$

On addition of a solution of silver nitrate to a neutral solution of the ammonium salt of phenylglutaric acid a white, amorphous precipitate of the silver salt is obtained that is almost insoluble in hot water. It does not change on exposure to the light, and may be dried at 100°; 0.6747 gram of air-dried salt did not change in weight on heating to 100° C., and gave 0.3443 gram silver.

	Calculated for $C_{11}H_{10}Ag_2O_4$.	Found.
Ag	51.18	51.32

The following qualitative reactions of the acid were obtained by adding solutions of the salts to an aqueous solution of the ammonium salt:

$CuSO_4$: Blue, amorphous precipitate, difficultly soluble in hot water.

$Pb(C_2H_3O_2)_2$: White, amorphous precipitate. On heating in presence of water, it is converted into bundles of small, truncated prisms, slightly soluble in water.

$HgNO_3$: A precipitate of white discs that are insoluble in hot water.

$Hg(NO_3)_2$: In the cold no change was noticed, but on heating the solution a granular precipitate was deposited.

$SnCl_2$: A precipitate of large, colorless, striated, flat prisms, with obliquely truncated ends, soluble in hot water.

$FeCl_3$: Amorphous, salmon-colored precipitate, insoluble in hot water.

Barium and magnesium chlorides gave no precipitate.

Action of Sodium Acetacetic Ether on Cinnamic Ether.

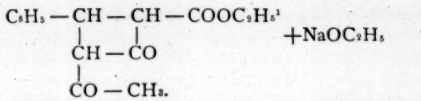
2.6 grams sodium were dissolved in 30 grams absolute alcohol, 14.8 grams acetacetic ether and finally 20 grams cinnamic ether were added. The solution was allowed to stand for five minutes, and then heated on the water-bath until the greater part of the alcohol was driven off. On treating the residue with water an oil remained undissolved that was removed by extracting with ether. The aqueous solution was then acidified, when a very heavy, oily substance separated, that gradually turned solid. A partial purification of this substance may be effected by extracting with ether immediately after acidifying, when it goes into solution, to partially separate soon after as white needles. The filtrate from these needles contained a notable amount of the substance that may be obtained by evaporation, or better by drying the solution with fused calcium chloride, when the substance is almost completely precipitated. For analysis it was purified by one crystallisation from dilute and two from strong alcohol.

0.2452 gram substance gave 0.6227 gram CO_2 and 0.1402 gram H_2O.

	Theory for $C_{13}H_{14}O_4$.	Found.
C	69.23	69.29
H	6.15	6.35

The substance crystallises from alcohol as long, white needles that melt at 140°–141°. It is insoluble in water, quite soluble in alcohol, and moderately in moist ether, but almost insoluble in the latter solvent when dry. It possesses acid properties, dissolving in alkalies and hot solutions of the alkali carbonates. The formation of this compound may be represented as follows:

$$C_6H_5-CH-CH-COOC_2H_5 + CH_3-CO-CHNa-COOC_2H_5 = C_6H_5-CH-CHNa-COOC_2H_5$$
$$\qquad\qquad\qquad



The silver salt was obtained by adding a solution of silver nitrate to a neutral solution of the substance in ammonia. It separated as radial clusters of small white prisms that are insoluble in water. The salt is extremely sensitive to exposure to the light, and decomposes when heated to 100° C.

0.6616 gram salt dried in a vacuum gave 0.1906 gram silver.

	Theory for $C_{18}H_{18}AgO_4$.	Found.
Ag	29.41	28.83

The following qualitative reactions were obtained by adding aqueous solutions of metallic salts to a neutral solution of the substance in ammonia: $Cu(NO_3)_2$: Green, amorphous precipitate, insoluble in hot water, but softening under it; $SrCl_2$: White precipitate of globular groups of small prisms, insoluble in hot water; $HgCl_2$: White, granular precipitate, insoluble in water; $Pb(NO_3)_2$: White, amorphous precipitate, moderately soluble in hot water, but softens under it when an insufficient amount of water is used; $FeCl_3$: Dark brown precipitate, difficultly soluble in hot water.

Barium and magnesium chlorides give no precipitate.

Action of Sodium Acetacetic Ether on Citraconic Ether.

It seemed of interest to ascertain whether the ethers of unsaturated fatty acids possess the property of adding to sodium acetacetic ether, and a few preliminary experiments with citraconic ether were made. To a solution of 2.6 grams of sodium in 30 grams of absolute alcohol, 15 grams of acetacetic ether, and then, after cooling, 21.4 grams of citraconic ether were added. The solution was heated on a water-bath until most of the alcohol was expelled, and the residue treated with water; an oil remained undissolved, and by acidifying a further quantity of an oily substance separated.

[1] This compound is isomeric with the cinnamyl acetacetic ether obtained by Fischer and Kuzel (Berichte d. deutsch. chem. Gesell. **16**, 166) by the action of cinnamyl chloride on sodium acetacetic ether. Experiments with this compound, and analogous substances from other unsaturated ethers, the results of which will be published later, show quite definitely that sodium and $COOC_2H_5$ when in the γ-position—and, as the following paper shows, also in the δ-position—have a great tendency to condense by eliminating C_2H_5ONa. I intend to follow up this subject, which promises extremely interesting results. I shall endeavor to bring further proof of the correctness of the formula given above.

The ethereal extract of this mixture contained two substances that were separated by repeatedly shaking with a solution of sodium carbonate. After drying the ethereal solution over calcium chloride, the ether was distilled off, and an attempt was made to fractionate part of the residue under ordinary pressure, but, as it decomposed considerably under these conditions, a pure substance was not obtained. The remainder was fractionated four times in a vacuum, when most of the liquid passed over between 170°–180°; and finally a colorless oil was obtained that boiled at 173°–174° under 26 mm. pressure (oil-bath, 235° thermometer to 40° in vapor).

0.2871 gram oil gave 0.6033 gram CO_2 and 0.1989 gram H_2O.

0.2861 gram oil gave 0.6056 gram CO_2 and 0.1992 gram H_2O.

	Theory for $C_{13}H_{24}O_7$.	Found.	
C	57.00	57.39	57.66
H	7.59	7.71	7.74

The neutral substance is formed by direct union of reagents:

$$C_3H_4=(COOC_2H_5)_2+CH_3CO-CHNa-COOC_2H_5=C_{13}H_{23}NaO_7,$$

$$C_{13}H_{23}NaO_7+H_2O=C_{13}H_{24}O_7+NaOH.$$

The alkaline solution obtained by shaking the ethereal solution of the products of the reaction with sodium carbonate contains a substance with acid properties that is precipitated as a heavy oil on addition of a mineral acid. This substance could not be obtained in a solid state, and an attempt to purify it by fractionation in a vacuum failed, as it underwent partial decomposition. It has an odor like that of crotonic acid, and doubtless corresponds to the acid substance obtained by the action of cinnamic ether on sodium acetacetic ether.

Action of Sodium Malonic Ether on α-Bromacrylic Ether.

The action of ethylene bromide on sodium or disodium malonic ether gives rise to the same compound, called by its discoverers vinaconic or trimethylene-dicarboxylic ether. According to Fittig,[1] the substance possesses the constitution of a vinylmalonic ether, $CH_2-CH-CH(COOC_2H_5)_2$; while Perkin[2] considers it a derivative of trimethylene $\begin{matrix}CH_2-CH_2\\ \diagdown\ \diagup\\ C-(COOC_2H_5)_2\end{matrix}$. Somewhat later

[1] Fittig and Röder, Annalen der Chemie **227**, 13.

[2] Berichte d. deutsch. chem. Gesell. **17**, 53.

Conrad and Guthzeit[1] examined the behavior of $\alpha\beta$-dibrompropionic ether towards disodium malonic ether and obtained a compound that they considered, adopting the view of Perkin of the nature of these reactions, as trimethylene-tricarboxylic ether. The acid obtained by saponification decomposes on heating, forming what is called the trimethylene-dicarboxylic acid. Adopting Fittig's view of the constitution of vinaconic acid, the compounds of Conrad and Guthzeit are not derivatives of trimethylene, but unsaturated acids, and the dibasic acid has the same constitution as itaconic acid. They are, therefore, allo-isomeric.[2] This view of the reaction I attempted to prove by investigating the action of α-bromacrylic ether on sodium malonic ether, as the synthesis of Conrad's trimethylene-tricarboxylic ether in this way, judging from what was known at the time of the experiment, would conclusively prove that Fittig's view is the correct one. If we consider, however, that α-bromacrylic ether is an unsaturated substance, we shall have to take the newly discovered property that such substances have of adding to sodium malonic ether into consideration; and no less than three constitutions are possible for the compound in question:

$$\text{I. } CH_2-CBr-COOC_2H_5 + CHNa-(COOC_2H_5)_2 = CH_2-CH-(COOC_2H_5)_2.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CBrNa-COOC_2H_5$$

$$CH_2-CH-(COOC_2H_5)_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad + C_2H_5OH =$$
$$\quad | \qquad\quad CBrNa-COOC_2H_5$$

$$CH_2-CH-COOC_2H_5 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad + C_2H_5ONa =$$
$$\quad | \qquad\quad CBrH-COOC_2H_5$$

$$\alpha. \quad CH-CH-(COOC_2H_5)_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad + C_2H_5OH + NaBr.$$
$$\qquad\quad | \qquad\quad CH-COOC_2H_5$$

$$CH_2-CNa-(COOC_2H_5)_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad + C_2H_5OH =$$
$$\quad | \qquad\quad CHBr-COOC_2H_5$$

$$\beta. \quad CH_2-C-(COOC_2H_5)_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad + C_2H_5OH + NaBr;$$
$$\qquad\quad | \qquad\quad CH-COOC_2H_5$$

[1] Berichte d. deutsch. chem. Gesell. **17**, 1186.

[2] Michael, Berichte d. deutsch. chem. Gesell. **19**, 1385, 1378; **20**, 554; Michael and Browne, *ibid.* **19**, 1381; **20**, 550; Journal für prak. Chemie, [2] **35**, 257.

II. $CH_2-CBr-COOC_2H_5 + CHNa-(COOC_2H_5)_2 =$

$$\begin{array}{l} CH_2Na \\ | \\ CBr-CH-(COOC_2H_5)_2 = \\ | \\ COOC_2H_5 \end{array}$$

$$\begin{array}{l} CH_2 \\ | \\ C-CH-(COOC_2H_5)_2 + NaBr. \\ | \\ COOC_2H_5 \end{array}$$

α-Bromacrylic ether was made by Wagner and Tollens[1] by the action of ethyl bromide on silver bromacrylate, but as this method does not give very satisfactory results, I made several experiments to obtain it in a different manner. A solution of $\alpha\beta$-dibrompropionic ether in absolute alcohol was treated with the equivalent quantity of sodium ethyl oxide, when a violent reaction took place, and sodium bromide was deposited. The alcoholic solution was treated with water, extracted with ether, and dried over calcium chloride. On fractionating this extract it is easy to isolate a heavy, oily, colorless liquid, that is insoluble in water, and boils from 202°–204° under slight decomposition. The bromine determinations gave the following figures:

I. 0.3576 gram liquid gave 0.3137 gram AgBr.

II. 0.3845 gram liquid gave 0.3379 gram AgBr.

	Theory for $C_7H_{13}O_2Br$.	Found.	
Br	37.3	37.05	37.14

The liquid is formed by replacement of bromine by ethoxyl, and is α-ethoxy-β-brompropionic ether:

$$CH_2Br-CHBr-COOC_2H_5 + NaOC_2H_5 = CH_2Br-CH(OC_2H_5)-COOC_2H_5 + NaBr.$$

Another experiment was to heat dibrompropionic ether to a high temperature in a paraffin-bath. Heated somewhat below the boiling-point of the ether, an evolution of bromhydric acid took place, but it was found impossible to isolate α-bromacrylic ether from the resulting product. These experiments having failed, I returned to the method of Wagner and Tollens, that I found of advantage to slightly modify. The silver salt and an excess of ethyl bromide were heated in a closed tube for six hours at 100°, and the

[1] Annalen der Chemie **171**, 350.

tube was then opened, connected with a condenser and heated on a water-bath until the excess of the bromide was expelled. The apparatus was now connected with an air-pump, the air exhausted from it, and the tube heated in a Meyer's air-bath as long as a liquid passed over. On fractionating the distillate in a vacuum it is easy to isolate a light oil that distils without decomposition between 75°–77° under 33 mm. pressure.

0.4551 gram substance gave 0.4875 gram of AgBr.

	Theory for $CH_3-CBr-COOC_2H_5$.	Found.
Br	44·7	45·53

Ten grams of α-bromacrylic ether were gradually added to a solution of sodium malonic ether, prepared by adding a solution of 1.1 grams of sodium in absolute alcohol to 7 grams of malonic ether. The reaction was violent, and the solution gave no alkaline test after it had stood a short time. The flask containing the product of the reaction was heated on a water-bath until most of the alcohol was driven off, the residue mixed with water and extracted with ether. On fractionating, after the ether had passed over, the thermometer rose very rapidly to 270°, when, between that temperature and 280°, almost the entire product of the reaction distilled. By fractionating this liquid[1] several times, it was easy to separate a fraction, that formed the greater part of the original liquid, boiling between 276°–277°. On analysis this portion gave the result as below:

	Theory for $C_{13}H_{18}O_4$.	Found.
C	55.81	55.60
H	7.00	7·34

The ether obtained from α-bromacrylic ether and sodium malonic ether agrees exactly in its properties with the compound obtained by Conrad and Guthzeit from $\alpha\beta$-dibrompropionic ether and disodium malonic ether; but, in order to give further proof of the identity of the two products, the first-named ether was saponified, and the acid so obtained compared with that described by Conrad and Guthzeit. The decomposition of the ether by aqueous sodium

[1] I have used for upwards of a year a slightly modified Hempel column that deserves a brief description. A round glass bulb that goes loosely into the neck of the fractionating flask, and is open at both ends, is attached to a piece of thin platinum wire and suspended from the top of the flask so that it is half-way in the neck and round part. The neck is then almost filled to the lateral tube with beads, and the distillation effected as usual. It is astonishing how much sharper a few inches of beads will cause a separation of two liquids than without their use. By using a long-neck boiling flask, a good Hempel column can be arranged in the flask.

hydrate gave an acid which, though finally obtained pure, is difficult to purify. A better result is obtained by decomposing with barium hydrate. For this purpose the ether was boiled several hours, in a flask with a reverse condenser, with a concentrated aqueous solution of three times the theoretical quantity of base. As the ether was decomposed the insoluble barium salt of the acid was deposited. A sufficient quantity of chlorhydric acid to dissolve the salt was then added, the barium precipitated by sulphuric acid, and the filtrate repeatedly extracted with ether. On evaporation of the ether an oil remained that gradually solidified. Instead of crystallising from water and ether, it is more advantageous to purify by several crystallisations from glacial acetic acid. The acid obtained in this way melts between 184°–185°, under evolution of carbonic anhydride. It is obtained from water as hard, glittering prisms, forming concentric groups, with end faces, which are sometimes not well defined, giving a navicular shape to the crystals. I also made the acid according to the method of Conrad and Guthzeit, and found that the properties of their product correspond exactly with those which I have just described. The neutral solutions of the acid in ammonia also gave the same qualitative tests on addition of various salts. These experiments seem to me to prove quite conclusively that α-bromacrylic ether and sodium malonic ether[1] and $\alpha\beta$-dibrompropionic ether and disodium malonic ether react to form the same compound.

According to Perkin, vinaconic ether does not contain a hydrogen that can be substituted by sodium. It seemed of interest to examine trimethylene-tricarboxylic ether in its behavior towards sodium ethyl oxide and alkyl halogens, and it was found that the ether obtained by using $\alpha\beta$-dibrompropionic ether gave the same result as that made with α-bromacrylic ether. On adding the ether to an absolute alcoholic solution of sodium ethyl oxide, the reagents being used in equivalent proportions, the solutions turned slightly yellow, which would seem to indicate that the ether contains a hydrogen replaceable by sodium. If such a compound be formed,

[1] The bromine estimation of α-bromacrylic ether given above is somewhat high; and as it might seem that the so-called trimethylene-tricarboxylic ether was formed from some $\alpha\beta$-dibrompropionic ether contained in it, I mention the quantitative results obtained in my experiment. Ten grams α-bromacrylic ether gave seven grams of ether boiling between 276°–277°, and three or four grams that were almost pure. If the bromacrylic ether contained 5 per cent. of the dibromether, the bromine percentage would have been increased 1 per cent., and only one gram of the ether boiling at 277° could have been formed. The high bromine percentage is undoubtedly caused by a trace of bromhydric acid that I found impossible to remove by distillation.

it is certainly very unstable, as by allowing ethyl iodide or benzyl chloride to react on the solution—although a separation of sodium iodide or chloride took place slowly in the cold, more rapidly on heating, and it lost its alkaline reaction—nothing but unchanged trimethylene-tricarboxylic ether could be isolated.

It evidently follows from the results described in this paper that the so-called trimethylene-tricarboxylic ether may possess one of three different constitutions, and to none of these can a decided preference be given at present.

In the present paper only unsaturated ethers were examined in which the unsaturated carbons are in the α- and β-position towards the carboxylic ether group. I shall make the behavior of other classes of unsaturated ethers and of the bromalkylenes the subject of a future paper.[1]

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ON SOME NEW REACTIONS WITH SODIUM ACETACETIC AND SODIUM MALONIC ETHERS.

BY ARTHUR MICHAEL.

Although sodium acetacetic ether and analogous sodium compounds have been the starting-points of almost innumerable researches and have yielded some of the most interesting syntheses known in organic chemistry, it would seem as if the view presented in the preceding paper—that is, the dual nature of these compounds—has been overlooked. The results obtained by treating these sodium compounds with unsaturated organic ethers suggested the desirability of examining their behavior towards organic reagents that have the property of uniting with substances with weakly combined negative and positive components. This investigation has yielded such an extensive, in fact almost unlimited, field of investigation, that I deemed it desirable to publish a preliminary note on the results already obtained, reserving a full account of the work and its continuation for a future paper.

[1] It would also be of interest to examine the behavior of the sodium derivative of nitroethane towards unsaturated ethers.

Behavior towards Aldehydes.—Claissen[1] has found that by treating a mixture of an aldehyde and acetacetic or malonic ether with dehydrating agents a series of new compounds is formed with elimination of water. An entirely different series of compounds is obtained by allowing aldehydes to react on the sodium derivatives of these ethers. Thus, by allowing an alcoholic solution of benzoic aldehyde and sodium acetacetic ether to stand for a day, a compound crystallising in flat prismatic plates of the composition $C_{22}H_{22}O_7$ is formed:

$$C_6H_5CHO + CH_3COCHNa - COOC_2H_5 = C_{13}H_{15}NaO_4;$$
$$2C_{13}H_{15}NaO_4 = C_{22}H_{30}Na_2O_7 + (C_2H_5)_2O.$$

This compound melts at 126°–127° and is soluble in alkalies, while the compound obtained according to the method discovered by Claissen melts at 59° and is insoluble in alkalies.

Behavior towards Ketones.—This class of compounds does not react in the cold, but on heating at 100° in a closed tube crystalline salts are deposited. The reaction has not been further examined.

Behavior of Mustard Oils.—The alkyl and aromatic mustard oils unite very readily with sodium acetacetic and malonic ethers to form mono-thio-amides. Thus, by mixing phenyl mustard oils with alcoholic sodium malonic ether the latter compound goes immediately into solution, and soon rhombic prisms separate that have the composition $C_{14}H_{16}NaSNO_4$. By treating this salt with an acid the thio-anilide is obtained that crystallises in long yellow needles melting at 59½°–60°:

$$CHNa-(COOC_2H_5)_2 + C_6H_5NCS = CH\begin{matrix}\diagup CSNNaC_6H_5\\ \diagdown (COOC_2H_5)_2\end{matrix};$$

$$CH\begin{matrix}< CSNNaC_6H_5\\ (COOC_2H_5)_2\end{matrix} + HCl = CH\begin{matrix}\diagup CSNHC_6H_5\\ \diagdown (COOC_2H_5)_2\end{matrix}.$$

Behavior of Phenyl Isocyanate.—These reactions are more complicated than those of the corresponding mustard oils. In its action on sodium acetacetic ether two products and on the malonic salt three products are formed. The isocyanate reacted very violently on sodium malonic ether. After standing some hours the white salt was separated by filtration, and the filtrate acidified. The oil that separated solidified partially on standing, and the solid substance,

[1] Annalen der Chemie **218**, 12, 129 and 170; also Hantzsch, Berichte d. deutsch. chem. Gesell. **18**, 2579.

after crystallisation from alcohol, melted at 123°–124°, and is the mono-anilide of methenyl-diethyl-tricarboxylate:

$$CHNa-(COOC_2H_5)_2 + C_6H_5NCO = CH\begin{matrix}\diagup CONNaC_6H_5\\ \diagdown (COOC_2H_5)_2\end{matrix}.$$

The white salt yielded after treating with acids a compound crystallising in orange plates, and melting at 171½°–172°. Its composition is expressed by the formula $C_{15}O_3H_9N$, and it is probably formed from the preceding substance by splitting off of alcohol and water:

$$C_{14}O_5H_{17}N = C_{13}O_3H_9N + H_2O + C_2H_6O.$$

Behavior of Anhydrides of Bibasic Organic Acids.—The substances unite immediately, forming carbonyl acids. Thus, on mixing a warm alcoholic solution of phthalic anhydride with alcoholic sodium acetacetic ether the solution turns solid on cooling. From the sodium salt, by treating with an acid and extracting with ether, a heavy oil is obtained that was dried in a vacuum at 100°. This substance has acid properties, and decomposes at 140° into phthalic anhydride and acetacetic ether. Its composition is $C_{14}H_{14}O_5$:

$$C_6H_4\begin{matrix}CO\\ CO\end{matrix}O + CH_3-CO-CHNa-COOC_2H_5 =$$

$$C_6H_4\begin{matrix}CO-CH\\ COONa\end{matrix}\!\!<\!\!\begin{matrix}CO-CH_3\\ COOC_2H_5\end{matrix}.$$

Behavior of Inorganic Anhydrides.—Carbon dioxide passed through an alcoholic solution of sodium malonic ether causes a precipitate of the compound $CH\begin{matrix}\diagup COONa\\ \diagdown (COOC_2H_5)_2\end{matrix}$;

$$CO_2 + CHNa=(COOC_2H_5)_2 = CH\!<\!\begin{matrix}COONa\\ (COOC_2H_5)_2\end{matrix}.$$

This salt is very unstable, as even cold water decomposes it into malonic ether and sodium bicarbonate. Carbon bisulphide reacts immediately on sodium malonic ether, forming a yellow salt. Acids precipitate from a solution of the salt a heavy oil with a disagreeable odor:

$$2CHNa(COOC_2H_5)_2 + CS_2 =$$

$$CNa\begin{matrix}\diagup CSSNa\\ \diagdown (COOC_2H_5)_2\end{matrix} + CH_2(COOC_2H_5)_2.$$

Sulphur dioxide and sodium malonic ether also give a precipitate, that appears to consist of sodium ethyl sulphate:

$$CHNa=(COOC_2H_5)_2+SO_2+C_2H_5OH=$$
$$CH_2=(COOC_2H_5)_2+SO\begin{matrix}OC_2H_5\\ONa\end{matrix}.$$

A different result is obtained by treating solid sodium malonic ether suspended in benzene with sulphur dioxide. Under these conditions apparently a sulphinate is formed. Phosphorus pentoxide also acts on sodium malonic ether under the same conditions.

Behavior of Phenols.—By dehydrating a mixture of resorcin and acetacetic ether with zinc chloride, Schmid[1] obtained a beautifully fluorescent body, which he named resocyanine. The correct formula of this substance was afterwards ascertained by v. Pechman and Duisberg[2] and by myself.[3] Wittenberg[4] obtained similar compounds from other phenols and acetacetic ether, and v. Pechman and Duisberg proved that the substances belong to the coumarine series. The same class of derivatives is obtained by allowing an alcoholic solution of phenols and sodium acetacetic ether to stand in the cold. A solution of resorcinol in sodium acetacetic ether soon became fluorescent, and, after standing several days, it was diluted with water and acidified, when a copious precipitate of resocyanine or β-methylumbelliferone was formed. This reaction is remarkable on account of the condensations that take place in the cold:

$$C_6H_4\begin{matrix}OH\\OH\end{matrix}+CH_3-CO-CHNa-COOC_2H_5=$$
$$C_6H_3\begin{cases}OH\\OH\\COH-CHNa-COOC_2H_5\\|\\CH_3\end{cases}=$$
$$C_6H_3\begin{cases}OH\\ONa\\COH-CH_2-COOC_2H_5\\|\\CH_3\end{cases}=$$
$$C_6H_3\begin{cases}OH\\O\text{——}\\C-CH-CO\\|\\CH_3\end{cases}+NaOC_2H_5+H_2O.$$

[1] Journal f. praktische Chemie [2], **25**, 81.
[2] Berichte d. deutsch. chem. Gesell. **16**, 2119; v. Pechman and Cohen, *ibid.* **17**, 2129.
[3] This Journal **5**, 434. [4] Journal f. praktische Chemie [2], **26**, 66.

While working on resocyanine, I endeavored to make similar derivatives from resorcinol and malonic ether by means of zinc chloride, but was unable to obtain any results. By the action of resorcinol and sodium malonic ether a fluorescent compound is formed that has not as yet been further examined.

Behavior of Sulphur.—Flowers of sulphur dissolve in the cold in alcoholic sodium malonic ether, but apparently no reaction takes place. On heating this solution to 100° a crystalline precipitate is formed that when treated with acids gives a heavy oil, with a strong mercaptane odor.[1] This oil undoubtedly represents the thiotartronic ether:

$$CHNa=(COOC_2H_5)_2+S=CHSNa=(COOC_2H_5)_2.$$

Behavior of Ureas.—Sodium acetacetic and malonic ethers react on carbamides to form the corresponding ureides. As an example, the action of carbamide on sodium malonic ether may be mentioned. The finely powdered substance dissolves in alcoholic sodium malonic ether, and presently the solution becomes solid. This precipitate is the sodium salt of barbituric acid, which may be obtained from it by treating it with acids:

$$CHNa-(COOC_2H_5)_2+CO(NH_2)_2=$$
$$CHNa\begin{matrix}CO-NH\\CO-NH\end{matrix}>CO+2C_2H_5OH.$$

Behavior of Sulpho-urea.—This compound acts like urea to form the corresponding sulpho-derivatives. Thus, from sulpho-urea and sodium malonic ether a crystalline precipitate is formed that consists of sodium sulpho-barbiturate. The free acid forms rhombic plates, that decompose at a high temperature without melting:

$$CS(NH_2)_2+CHNa-(COOC_2H_5)_2=$$
$$CHNa\begin{matrix}CO-NH\\CO-NH\end{matrix}>CS+2C_2H_5OH.$$

Behavior of Amides.—Sodium derivatives, formed by elimination of alcohol, are deposited. Acetamide dissolves readily in alcoholic sodium malonic ether, in proportion of two molecules of the first to one of the second compound, and the solution soon solidifies. This compound crystallises in prisms and has the composition $C_7O_4N_2Na_2H_8$:

$$2CHNa-COOC_2H_5+2CH_3-CONH_2=C_7Na_2N_2H_5$$
$$+CH_2-(COOC_2H_5)_2+2C_2H_5OH.$$

[1] Sulphur dissolves in malonic ether and gives off hydrogen sulphide on boiling.

Behavior of Aldehyde-ammonia.—As in the preceding reaction, condensation-products containing sodium are formed. Aldehyde-ammonia dissolves readily in alcoholic sodium acetacetic ether, and in a few minutes the solution becomes solid. The substance, which crystallises in long, fine, white needles in alcohol, has the composition $C_8H_{12}O_3NNa$:

$$CH_3-CH\begin{matrix}OH\\NH_2\end{matrix}+CH_3-CO-CHNa-COOC_2H_5=$$
$$C_8H_{16}O_4NNa;\quad C_8H_{16}O_4NNa=C_8H_{12}NaO_3N+2H_2O.^1$$

I have made some other tests with sodium acetacetic and malonic ethers, and find that these reagents react on lactones, amidines, primary bases, guanidine, cyanamide, cyanic acid and benzoquinone. The above-described reactions will also be tried with sodium derivatives containing two atoms of sodium in their molecule, and with the sodium derivates of the nitro-alkanes.

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[1] The four last reactions are probably caused by the formation of derivatives having stronger acid properties than the original substances, and the formation of sodium compounds that are insoluble in alcohol. In order to test this hypothesis, I have made some experiments on the action of a mixture of oxalic ether and sodium ethylate on urea, phenylhydrazine, guanidine and aldehyde-ammonia, and find that this mixture acts exactly as sodium acetacetic or malonic ethers. The addition of oxalic ether to a solution of urea in alcoholic sodium ethylate immediately causes a dense white precipitate, which is the sodium derivative of parabanic acid:

$$\begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix}+CO\begin{matrix}NH_2\\<\\NH_2\end{matrix}+NaOC_2H_5=CO\begin{matrix}NH-CO\\<\\NNa-CO\end{matrix}+3C_2H_5OH.$$

By using phenylhydrazine a precipitate consisting of prisms is formed. This has the composition of $C_8H_8N_2NaO_3$:

$$\begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix}+C_6H_5N_2H_3+C_2H_5ONa=\begin{matrix}CO-N_2H_3C_3H_5\\|\\COONa\end{matrix}+2C_2H_5OH.$$

Guanidine and sodium ethylate treated with oxalic ether gave a heavy white precipitate containing 34 per cent. sodium. The salt treated with acids gives a crystalline substance which decomposes at a high temperature, and is almost insoluble in all solvents. This compound has the constitution $C_3N_3H_3O_2$, and is oxalylguanidine:

$$HN-C\begin{matrix}NH_2\\<\\NH_2\end{matrix}HSCN+\begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix}+NaOC_2H_5=$$
$$NH-C\begin{matrix}NH-CO\\<\\NH-CO\end{matrix}+NaSCN+3C_2H_5OH.$$

Other organic reagents behave in presence of sodium ethylate in a similar manner, as experiments with sulpho-urea, cyanamide, amidines and hydroxylamine have shown. There is no doubt that weakly defined basic or acid substances act as strong bases in the presence of sodium ethylate. Not alone oxalic ether acts in this manner, but carbonic, benzoic, succinic, and tartaric ethers act in the presence of sodium ethylate on most of the above reagents, forming new compounds. It is very likely that all organic ethers that do not undergo a change when mixed with sodium ethylate will give similar reactions. It has also been found that mixtures of sodium ethylate and weak bases behave towards certain other reagents as strong bases. This research will be continued.

ON THE ACTION OF ALDEHYDES ON PHENOLS. III.[1]

By A. Michael and J. P. Ryder.

In an earlier paper it was shown that benzoic aldehyde in the presence of a trace of a mineral acid acts on resorcinol, forming the resinous compound $C_{26}H_{20}O_4$, which is easily converted by mineral acids into an isomeric crystalline substance. In the present paper we have made the behavior of a number of aldehydes towards phenols the subject of a similar investigation.

Behavior of Benzoic Aldehyde towards Phenol.

Benzoic aldehyde heated with phenol does not act on it, but a reaction takes place when a small amount of hydrochloric acid is present. A solution of 15 grams phenol, 13.3 grams benzoic aldehyde, and five drops of hydrochloric acid dissolved in 20 grams of alcohol, was heated in an atmosphere of carbon dioxide for about an hour, and afterwards treated with steam in order to expel any unchanged aldehyde or phenol. A resinous substance remained behind, which we were unable to crystallise. For analysis it was dissolved in glacial acetic acid, and the solution poured into water, an operation which was repeated several times. The resin was dried in a vacuum at 100° and was analysed, with the following results:

0.211 gram substance gave 0.657 gram CO_2 and 0.102 gram H_2O.

	Theory for $C_{28}H_{20}O$.	Found.
C	85.71	84.90
H	5.49	5.37

The resin when pure is white, but a slight exposure to the air is sufficient to color it somewhat. The substance analysed was slightly colored, which accounts for the noticeable difference between the percentages indicated by theory and those obtained from the analysis. That, however, this substance has the above formula was shown by preparing its acetyl derivative. For this purpose 2 grams of the resin, 4 grams of acetic anhydride, and 1 gram of fused sodium acetate were heated on a water-bath, and then treated with water. The white, amorphous product was

[1] This Journal 5, 338 and 349. The work published in this paper was done in the winter of 1884.

purified by dissolving in acetic acid and precipitation by water. It gave the following numbers:

0.407 gram substance dried in a vacuum at 100° gave 1.119 grams CO_2 and 0.205 gram H_2O.

	Theory for $C_{24}H_{18}O_2(OCCH_3)_2$.	Found.
C	80.26	79.71
H	5.40	5.59

We were unable by treatment with acid to convert the resin into a crystalline substance. Distilled with zinc dust, a small amount of high-boiling hydrocarbons was obtained, but a fractional distillation of these products failed to isolate a homogeneous substance.

The resin is formed according to the equation:

$$2C_6H_6O + 2C_6H_5CHO = C_{26}H_{20}O_2 + 2H_2O.$$

Action of Benzoic Aldehyde on Pyrogallol.

The reaction between benzoic aldehyde and pyrogallol in the presence of considerable hydrochloric acid was examined by v. Baeyer,[1] who obtained, when operating in the cold, the resinous substance $C_{24}H_{22}O_7$, and in the heat an isomeric crystalline compound. The formation of this substance from two molecules of the aldehyde and phenol under elimination of a molecule of water did not conform with our experiences in the similar resorcinol reaction; but as v. Baeyer used a large quantity of strong acid, we thought the difference might be due to that fact. We therefore repeated v. Baeyer's experiment, and the results of our analyses lead us to change the constitution of the crystalline substance.

Pyrogallol and benzoic aldehyde were dissolved in absolute alcohol, the air of the vessel expelled by carbon dioxide, and concentrated hydrochloric acid added in small quantities. The first of the two following analyses was made with a portion of the substance formed as soon as acid was added to the solution, while for the second the compound obtained by adding considerable acid was crystallised from acetone. In each case the substance was dried in an atmosphere of carbon dioxide *in vacuo* at 100°, and the dry products were perfectly white.

I. 0.181 gram substance gave 0.479 gram CO_2 and 0.0795 gram H_2O.

II. 0.220 gram substance gave 0.585 gram CO_2 and 0.096 gram H_2O.

[1] Berichte d. deutsch. chem. Gesell. **5**, 25, 280.

	Theory for v. Baeyer's Formula, $C_{26}H_{22}O_7$.	Theory for $C_{26}H_{20}O_6$.	Found. I.	Found. II.
C	69.95	72.89	72.41	72.54
H	4.92	4.67	4.91	4.85

That the substance possesses the composition $C_{26}H_{20}O_6$ was further confirmed by preparing and analysing its acetyl derivative. For this purpose it was treated with acetic anhydride and sodium acetate at 100° C., and the product of the reaction crystallised from glacial acetic acid. An analysis gave the following numbers:

0.241 gram substance, dried at 100° in the air, gave 0.591 gram CO_2 and 0.104 gave H_2O.

Theory for $C_{26}H_{14}O_6(OCCH_3)_6$.	For v. Baeyer's Formula, $C_{26}H_{16}O_7(C_2H_3O)_6$.	Found.
67.05	62.75	66.88
4.70	4.78	4.79

The compound forms white, truncated prisms that may be heated to 100° C. in the air without change.

We have also convinced ourselves by experiments that the same substance is formed by treating the alcoholic aldehyde-pyrogallol solution with a small amount of acid; and that the formation of the crystalline substance is preceded by that of an amorphous substance, which by heating with acid is changed into the crystalline isomeride. In fact the reaction is strictly analogous to that of resorcinol, although with pyrogallol it was found that relatively more acid is required to form the resin, and also for its conversion into the crystalline modification.

Action of Benzoic Aldehyde on Phloroglucinol.

A drop of hydrochloric acid added to a boiling alcoholic solution of the phenol and aldehyde causes an immediate precipitate of a resinous compound which is quite insoluble in alcohol. For analysis it was dissolved in hot alcohol, and the precipitate obtained by cooling dried at 100° in a vacuum.

0.221 gram substance gave 1.586 grams CO_2 and 0.092 gram H_2O.

	Theory for $C_{26}H_{20}O_6$.	Found.
C	72.89	72.31
H	4.67	4.62

The resin is very susceptible to oxidation, turning quickly red in the air. We were unable to convert this substance into the

crystalline modification. An alcoholic solution treated with a considerable quantity of acid gave unchanged resin.

Action of Benzoic Aldehyde on Orcinol.

Ten grams of orcinol, 8.5 of aldehyde, 15 of absolute alcohol and two drops of hydrochloric acid were heated for a short time, and the solution thrown into water. The white resin that was precipitated was purified by dissolving in alcohol and precipitating with water. For analysis it was dried in carbon dioxide at 100°.

0.232 gram resin gave 0.672 gram CO_2 and 0.120 gram H_2O.

	Theory for $C_{22}H_{24}O_4$.	Found.
C	79.23	78.95
H	5.66	5.76

Like most of the analogous compounds, it is easily oxidised in the air. This resin could not be converted into a crystalline compound. It was found to remain unchanged even when boiled with strong hydrochloric acid.

Qualitative Experiments on the Behavior of Phenols towards Aldehydes.

In the following experiments the phenol and aldehyde were dissolved in absolute alcohol and a small quantity of hydrochloric acid was added. Hydroquinol and benzoic aldehyde do not react in the cold, but after heating the solution the addition of water precipitates a resin.

Eugenol and Benzoic Aldehyde.—No reaction even on boiling the solution and adding a considerable amount of acid.

α-Naphthol and Benzoic Aldehyde.—Violent reaction in the cold. On pouring into water a resin was precipitated.

β-Naphthol and Benzoic Aldehyde.—Converted into a resin after standing some hours.

Hydroquinol and Ethyl Aldehyde.—No resin formed in the cold, but on heating.

Eugenol and Ethyl Aldehyde.—No resin formed in the cold nor in the heat.

Pyrogallol and Ethyl Aldehyde.—No reaction in the cold. On heating a resin is formed.

Resorcinol and Butyric Aldehyde.—Resin formed in the cold.

Resorcinol and Valeric Aldehyde.—Resin formed in the cold.

Resorcinol and Œnanthol.—Resin formed in the cold. Could not be converted into a crystalline substance.

Resorcinol and Cinnamic Aldehyde.—Immediate reaction in the cold. The resin remained unchanged on further treatment with acid.

Resorcinol and Cuminol.—Resin formed in the cold that is convertible into a crystalline substance consisting of square plates.

Resorcinol as a Reagent for the Detection of Aldehydes.

The above-described experiments, together with those described in the former paper on this subject, show that an absolute alcoholic solution of resorcinol containing a trace of hydrochloric acid would be a valuable reagent for detecting aldehydes of monobasic acids, if no other analogous substances show a similar behavior. We have examined chloral hydrate, acetone, benzophenone, butyrone, acetacetic ether, acetophenone, mesoxalic and pyruvic acids, in regard to their behavior towards the resorcinol solution, and find that no reaction takes place in the cold, even if considerable acid is added. No reaction takes place when succinic or phthalic anhydrides or dextrose and levulose are added to the solution.

In testing for an aldehyde we recommend a solution of one part of resorcinol in two of absolute alcohol, then the addition of a small amount of the substance to be tested, and finally a few drops of strong hydrochloric acid. If no resin is formed, the solution, after standing several hours, is poured into water, when, if the substance contains an aldehyde, a resinous or crystalline precipitate should be formed.[1] This test is of special interest, inasmuch as it distinguishes an aldehyde from a ketone, while such reagents as hydroxylamine and phenylhydrazine give tests for both these groups of substances. By combining the resorcinol test with one of the above, it may be ascertained whether the substance contains a ketone, as, if a substance gives the two last tests and not the first, it must evidently be due to the presence of a ketone.

Action of Chloral Hydrate on Orcinol.

In the second paper[2] on the action of aldehydes on phenols, it was shown that chloral hydrate and resorcinol, in aqueous solution, react in the heat to form a substance free of chlorine. This

[1] We have not tried the reaction on other classes of aldehydes.

[2] This Journal **5**, 349.

substance is so unstable towards oxygen that a colorless specimen could not be obtained for analysis, and the formula deduced from the analytical results was open to some doubt. We thought it likely that the corresponding orcinol derivative would show a greater stability, and that its analysis might be of value in ascertaining the constitution of the resorcinol compound.

A solution of ten parts orcinol, five parts chloral hydrate in forty parts of water was heated to boiling, in a flask with a reversed condenser, and in an atmosphere of carbon dioxide, as long as the deposition of a crystalline substance was noticed. The precipitate was dissolved in hot dilute alcohol, treated with boneblack, and purified by several crystallisations. The substance was dried in a vacuum at 100°, and was very nearly white. On analysis it gave the numbers given below:

I. 0.212 gram substance gave 0.502 gram CO_2 and 0.101 gram H_2O.

II. 0.207 gram substance gave 0.488 gram CO_2 and 0.099 gram H_2O.

	Theory for $C_{22}H_{24}O_8$.	Found. I.	Found. II.
C	64.25	64.58	64.33
H	5.13	5.29	5.34

The compound crystallises from alcohol in white needles, which are insoluble in hot water, readily soluble in strong alcohol. It oxidises in the air, but is more stable than the resorcinol compound. By treating it at 100° with acetic anhydride and fused sodium acetate, an acetyl derivative was obtained. This substance was purified by crystallisation from alcohol, and melts at 185°. For analysis it was dried in the air at 100°.

0.196 gram gave 0.458 gram CO_2 and 0.090 gram H_2O.

	Theory for $C_{36}H_{34}O_{12}$.	Found.
C	63.42	63.73
H	5.13	5.10

The formation of a substance having the position $C_{22}H_{24}O_8$ from orcinol and chloral hydrate may be explained by assuming that the chlorine of the chloral hydrate acts on the hydrogen of the benzene nucleus, and the reaction may be represented as follows:

$$CCl_3CH(OH)_2 + 3C_6H_3(OH)_2CH_3 =$$
$$C[C_6H_2(OH)_2CH_3]_3 - CH(OH)_3 + 3HCl.$$

The substance may be considered as derived from the unstable ethylidene hydrate by the replacement of hydrogen by orcinolyl, and may be named triorcinolylethylidene hydrate. The action of acetic anhydride consists not alone in the introduction of acetyl, but also in dehydration:

$$C[C_6H_3(OH)_2CH_3]_3CH(OH)_2 + 7(C_2H_3O)_2O =$$
$$C[C_6H_2(OOCCH_3)_2CH_3]_3 - CHO + 8CH_3COOH.$$

These results induced us to analyse the resorcinol derivative again. We were unable to obtain a product that was not somewhat oxidised, owing to its great avidity for oxygen.

0.168 gram gave 0.394 gram CO_2 and 0.063 gram H_2O.

0.158 gram gave 0.3705 gram CO_2 and 0.062 gram H_2O.

	Theory for $C[C_6H_3(OH)_2]_3 - CH(OH)_2$.	Found.	
C	62.18	63.94	63.98
H	4.66	4.17	4.36

We are inclined to think that the discrepancy between the results indicated by theory and those obtained from analysis is due to the impossibility of obtaining a substance not partially oxidised. This view is corroborated by comparing the results obtained from the analysis of the perfectly stable derivative formed by the action of acetic anhydride and those required by theory:

	Calculated for $C[C_6H_2(OOCCH_3)_2]CHO$.	Found.	
C	61.93	61.71	61.70
H	4.51	4.32	4.67

An experiment was made to oxidise the acetyl derivative of the resorcinol compound. 2.5 grams of the substance were dissolved in cold acetic acid, and .66 gram of potassium permanganate, also in solution, gradually added. After standing 24 hours the solution was poured into water, and the precipitate thus formed crystallised several times from acetic acid.

0.221 gram, dried at 100° in the air, gave 0.509 gram CO_2 and 0.081 gram H_2O.

	Theory for $C_{20}H_{14}O_8$.	Found.
C	62.5	62.8
H	4.1	4.1

The substance crystallises in prisms that are insoluble in alcohol and water and melt at about 210°. It may be supposed to be formed by the oxidation of formyl into carboxyl and replacement of acetyl by hydrogen:

$$C_{20}H_{14}O_8 = C[C_6H_3(OH)_2]COOH.$$

Before this view can be wholly accepted a more detailed examination of the substance is necessary.[1]

TUFTS COLLEGE, COLLEGE HILL, MASS.

[1] Herr L. Claissen has recently published a paper (Berichte d. deutsch. chem. Gesell. **19**, 3316, and Annalen der Chemie **237**, 261), from v. Baeyer's laboratory, on the action of aldehydes on phenols, in which he takes occasion to criticise my work and publicly call attention to supposed negligence on my part in not acknowledging work done in the same laboratory. I gather from his remarks that Herr Claissen deems it proper to criticise the work of other chemists without becoming acquainted with their papers. At least, I can think of no other explanation of Herr Claissen's attitude in regard to my work, as every research that had been published on the subject in question from v. Baeyer's laboratory is given even a detailed mention in my paper (this Journal **5**, 338). Herr Claissen will find on consulting my paper that I have not relied on the proximate analyses of the resorcinol-benzoic aldehyde compounds to settle their constitution. Although the new formula he suggests for the resorcinol-benzoic aldehyde compound has a carbon and hydrogen percentage that approximates those obtained by analysis, the acetyl-derivate of such a compound differs very considerably in its carbon percentage from what was actually obtained, as will be seen from the following:

	Theory for Claissen's Formula of Resorcinol Compounds, $C_{19}H_{14}O_3$.	For my Formula, $C_{26}H_{20}O_4$.	Found. I.	II.	III.
C	78.62	78.69	78.32	78.83	78.78
H	4.81	5.05	5.27	5.62	5.51

	Theory for Acetyl-derivate of Claissen's Formula, $C_{19}H_{13}O_3(C_2H_3O)_2$.	For Acetyl-derivate of my Formula, $C_{26}H_{16}O_4(C_2H_3O)_4$.	Found.	
C	73.79	72.34	72.16	72.31
H	4.75	4.93	5.48	5.17

	Theory for Claissen's Formula of Pyrogallol Compound, $C_{19}H_{12}O_5$.	This Formula Less One Mol. of Water, $C_{19}H_{10}O_4$.	For Baeyer's Formula, $C_{26}H_{22}O_7$.	For my Formula, $C_{26}H_{20}O_4$.	Found.	
C	70.80	75.00	69.95	72.89	72.41	72.54
H	4.34	3.75	4.92	4.67	4.91	4.85

Theory for Claissen's Formula of Acetyl Derivative, $C_{19}H_8O_5(C_2H_3O)_4$.	Acetyl Derivative of $C_{19}H_{12}O_4$, $C_{19}H_8O_4(C_2H_3O)_2$.	Acetyl Derivative of Baeyer's Formula, $C_{26}H_{16}O_7(C_2H_3O)_6$.	Acetyl Derivative of my Formula, $C_{26}H_{14}O_8(C_2H_3O)_8$.	Found.
66.39	71.50	62.75	67.05	66.88
4.09	3.71	4.78	4.70	4.79

The figures speak for themselves, and I should make no further mention of the matter if Herr Claissen had not announced his intention to repeat my work. I should be pleased to have him do this, but I wish that he would consult my paper before he publishes his results, so as to prevent any further misrepresentation of my work on his part. Herr Claissen will find that my work was not done with a view of mere compound-making; that the work he has in view, and many other suggestions on the subject, were clearly stated a number of years before he began his work, and also that, until I published my research, the subject I examined rested on an entirely false basis. Nobody who takes the trouble to read the literature on the subject of aldehyde-phenol-condensation can for a moment doubt that those condensations that take place in so dilute an acid solution that the reactions might be used as tests for traces of mineral acids are different in their nature from those requiring the strongest known dehydrating agents, especially as entirely different results are obtained by using the different methods.

REVIEWS AND REPORTS.

ZEITSCHRIFT FÜR PHYSIKALISCHE CHEMIE, STÖCHIOMETRIE UND VERWANDTSCHAFTSLEHRE. Edited by WILH. OSTWALD and J. H. VAN'T HOFF. Leipsic. 12 numbers to the volume.

The interesting results derived from a so-called "cross-fertilisation of the sciences" are nowhere more apparent than in the field covered by both chemistry and physics. The phenomena of heat, light, electricity, vapor tension, crystallisation and density have all contributed to the problems of chemical energy; and the interest in these researches has so extended in late years that the new journal must find a cordial welcome. The editors (who have shown marked ability in quantitative experimental research, as well as mathematical analysis) are the authors of a "Lehrbuch der allgemeinen Chemie" and "Études de Dynamique chimique"; and these representatives of Russia and Holland at the head of a German periodical suggest the cosmopolitan character of science.

The first two numbers were issued in February and March. An introductory note quotes the remark of Du Bois-Reymond that "physical chemistry may be called the chemistry of the future." The journal is supplementary to Ostwald's text-book of "general chemistry"; for this, he says, in contrast to the special chemistry of the several kinds of matter, "is not merely a limb, but the sap of the tree."

The ninety-six pages already issued are chiefly devoted to original papers, the general purpose of which may be gleaned from the following summary:

P. C. F. Frowein. "Dissociation of Salts containing Water of Crystallisation." The vapor tensions of partly dehydrated salts are determined, and discussed in the light of thermodynamics.

O. Lehmann. "Crystallisation of Mixtures." After an historical introduction, and brief reference to his former debate with Dr. Brügelmann, a description is given of crystals of the four ethers: $C_4H_4O_2(CO.O.C_2H_5)_2$, $C_4H_6O_2(CO.O.C_2H_5)_2$, $C_6H_2(OH)_2(CO.O.C_2H_5)_2$ and $C_6(OH)_4(CO.O.C_2H_5)_2$; besides crystals containing each one mixed with each of the others.

L. F. Nilson and *Otto Pettersson.* "Physical Constants of Germanium and Titanium." The mean value for the atomic heat of Ti was normal from 0° to 211°, but lower from 0° to 100°, and much higher at 301.5° or 440°; that of Ge was nearly constant, a unit below normal, within the same range of temperatures. Determinations of vapor density showed a partial dissociation of GeI_4 at 658°, and probably of Ge S at a white heat. The critical temperature of $GeCl_4$ was 276.9°; and the vapor tension was determined for various temperatures.

D. Konowalow. "Theory of Fluids." The formula published by Van der Waals in 1881 to express "the continuity of the gaseous and fluid conditions" is discussed in regard to more recent experimental data and shown to be approximately correct.

W. Ostwald. "Nature of Chemical Affinity." Of the two isomeric nitrosalicylic acids, that having the constitution COOH : OH: $NO_2 = 1:2:3$ is decidedly stronger than that represented by 1 : 2 : 5. The hydroxyl is ortho and the nitro group is meta to carboxyl in both cases; hence the difference can only depend upon the different relations of the nitro and hydroxyl groups to each other.

D. Konowalow. "Decomposition of Tertiary Amyl Acetate." In continuation of the author's investigation of "contact action," he shows that the presence of acetic acid promotes the separation of the ether into this acid and amylen. Menschutkin's determinations of the speed of dissociation (1882) are thus explained.

Robert Schiff. "Coefficient of Expansion of Gases, as Quantitative Lecture Experiment." Description of apparatus, with cut.

St. Gniewosz and *Al. Walfisz.* "Absorption of Gases by Petroleum." The coefficients at 10° and at 20° for H, N, O, N_2O, C_2H_4, CO_2, CO, and CH_4 were determined; and at 20° nearly all were much *higher* than the coefficients for absorption by water; hence, a layer of petroleum seems to afford no adequate "protection" to aqueous solutions.

W. Meysztowicz. "Salts of Pyrosulphurous Acid." Those of Ca, Sr, Ba and Mg could not be obtained.

W. Ostwald. "Electro-chemical Studies. Fifth Paper: Law of F. Kohlrausch." The former papers (Jour. pr. Chem. 1884–1886) showed that the molecular conductivity of monobasic acids increases with dilution, and seems to approach the same maximum value with all the acids examined. Several hundred new determinations are now published, embracing fifteen acids and their salts, at different degrees of dilution. These show essential differences among the acids, but confirm Kohlrausch's theorem [Wied. Ann. **6**, 167, (1879)] that the conductivity of a salt is the sum of two constants, depending upon the nature of the acid and the base respectively. The mean value for the molecular conductivity of sodium salts is 21.1 higher than for the corresponding salts of potassium under like conditions of dilution; the conductivity of lithium salts being 9.7 higher still. Further data are promised, extending the observations to weaker acids.

R. B. WARDER.

ANALYSIS OF THE URINE. By K. B. HOFMANN and R. ULTZMANN. Translated by T. Barton Brune and H. Holbrook Curtis. New York: D. Appleton & Co., 1886.

Among the numerous smaller publications in the German language on the analysis of urine, the one by Hofmann and Ultzmann

occupies a deservedly high place. Its popularity in this country is attested by the appearance of a second edition of the English translation. In this later edition the necessary additions have been supplied to keep pace with the advances made during the past few years in the methods of analysis and the semiology of the urine.

Clearness of expression and the literary style show a marked improvement over the previous edition, although here and there the German idiom still persists.

The part descriptive of the normal and abnormal constituents of the urine with the qualitative tests is admirable. However, under the qualitative tests for albumen, the degree of delicacy of the picric acid test (Galippe's test) is stated to be above that of the nitric acid or the potassium ferrocyanide test. Laache, of Christiania, who made a thorough study of these tests, concludes that the nitric acid and the potassium ferrocyanide tests are of equal value, and that the picric acid test is considerably below them in delicacy.

Picric acid is also given as a test for glucose. The fact that picric acid in the presence of a caustic alkali produces similar claret-red colorations with either glucose or creatinine, and that it has even been brought forward as a delicate test for the latter in the urine, would hardly commend its employment as a good test for glucose.

Heller's or Moore's test is given as "the simplest and best test" for glucose. As the coloring matters in the urine so often interfere with this test, we may, by its performance, have the presence of glucose indicated in many urines which are entirely free from glucose.

Sufficient importance does not seem to have been given the tests for glucose with alkaline copper solutions.

To determine whether Fehling's solution has undergone decomposition, and is thereby unfit for use, it is advised simply to boil the Fehling's solution itself, neglecting to state that before boiling it should be diluted with about four volumes of water. Decomposition may have occurred in the Fehling's solution and without dilution before boiling would not become evident. This neglect is a fruitful source of error.

It is unfortunate that the methods for the preparation of the volumetric solutions are not given more in detail. Possessing the required standard solutions, the actual analysis is easily performed, as the methods for the latter are excellently and clearly described. It would, however, require a decidedly better knowledge of chemistry than is possessed by the average physician to prepare the standard solutions from the meagre descriptions given in the book, and also to accurately standardise them with solutions of known strength—which latter procedure is entirely omitted in this work.

The part devoted to the semiology of the urine is excellent, and must be of much value to the physician, while the plates showing the microscopic appearance of some of the normal and abnormal substances occurring in the urine cannot be excelled.

JOHN MARSHALL.

NOTES.

Apparatus for Filling a Burette.

The difficulty of filling a burette with standard solutions without a material loss of strength from evaporation has suggested to me the following plan: In Fig. 1, *A* is a glass tube bent as shown, and extending to the bottom of the bottle *C* containing the standard solution; *B* is a similar tube extending just beneath the stopper;

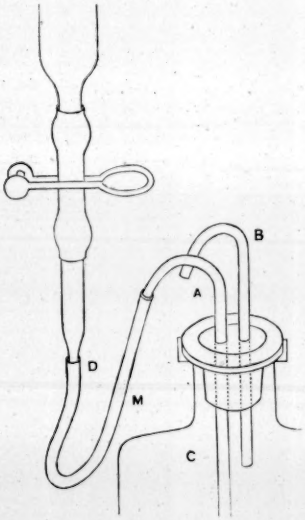

FIG. 1.

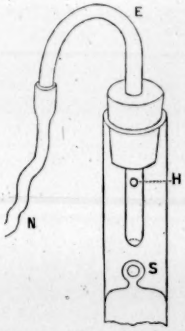

FIG. 2.

both tubes are sealed in the bottle after it is filled. A small rubber tube 30 cm. or 40 cm. long fits at either end on the glass tubes *A* and *B*, and remains in this position when the bottle is not in use. When the burette is to be filled the rubber tube is detached from *B* and slipped over the tip of the burette at *D*, thus leaving *B* open for the admission of air when the fluid is drawn from the bottle.

In Fig. 2, *E* is a bent glass tube fitted by means of a stopper to the top of the burette; it is pierced by a hole, *H*, in the side, just beneath the lower surface of the stopper, and extends about 2 cm. beyond, being open at each end; a rubber tube is attached to its outer end for the purpose of making suction with the mouth.

The bottle being attached by means of the rubber tube *M* to the tip of the burette, and the compressor being open, the fluid is drawn by suction on the tube *N* through the tube *A*, together with some air, into the burette. If a swimmer is not used, the air-bubbles will simply rise to the top and give no further trouble. With a swimmer, however, it will be necessary to remove them by drawing the swimmer forcibly against the bottom of the tube *E* (Fig. 2), when they will pass by the swimmer and escape; if not at the first trial, by allowing the swimmer to recede slightly and repeating the operation, the air will easily pass out. The object of extending *E* (Fig. 2) beneath the stopper, and of the lateral hole in *E*, is to prevent the solution from entering the suction tube *N*. When the burette is free from bubbles the fluid may be allowed to recede until the swimmer stands at the mark. The rubber tube *M* (Fig. 1) is detached from the burette and restored to its place on the tube *B*, thus sealing the bottle against any possible evaporation. The efficacy of the apparatus in preventing loss of strength is evident; in practice, I have found this method more speedy than any other I have known.

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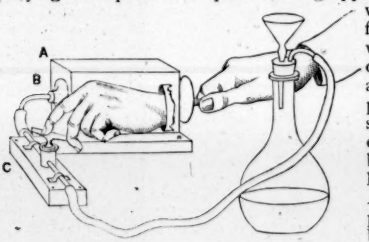
SOME PIECES OF CHEMICAL APPARATUS.

Simple, Portable, Quick-Filtering Apparatus.—The accompanying cut represents a quick-filtering apparatus devised by the writer some four or five years ago, and which, in the absence of a head of water, answers fully all the purposes of the Bunsen pump. *B* is an ordinary hard rubber syringe, 5 inches long, fixed in a block, *A* (which is a piece of pump stock with a bore to suit the diameter of the syringe, and screwed to the table); and *C* is a three-way stopcock worked with the left hand while the right hand works the piston of the syringe.



The idea was suggested by the text of Fleischer's volumetric analysis, Muir's translation, pp. 28 and 29, and the translator's note, p. 269, where devices inferior to this are described.

Sulphuretted Hydrogen Apparatus without Stray Fumes.—Kipp's apparatus is in every laboratory. When the apparatus is not in use, the acid is above the iron sulphide, and gravity tends to produce leakage. I put ferrous sulphide into the top instead of the middle globe, having filled the stem with broken porcelain. The bottom globe and one-half of the middle globe are then filled with dilute acid. To the tubulure of the middle globe (through which the gas is usually evolved) a rubber stopper, tube, and pinchcock are attached. By blowing through the tube the acid is made to ascend to the top globe, where it meets the iron sulphide.

When the gas is no longer needed, the pinchcock is opened and the acid falls. The evolution tube is connected with a wash-bottle, and the considerable difference of height renders regurgitation impossible.

Obviously, in the absence of Kipp's apparatus, the same principle can be variously applied. For example, a long bottle, say an inch and a half in diameter, may have its bottom cut off and a one-hole rubber stopper one and a half inches in diameter inserted. This, on being inverted, may take the place of the top globe of Kipp's apparatus, if a one-hole stopper and long tube be attached to the neck, and if another bottle with a two-hole stopper (one of the holes for the blowing-tube) be used as the acid reservoir.

Simple Arrangement for Reverse Filtration (*Carmichael's Plan*).—The neck of an ordinary vial is cut off. The outer end is ground on a lead, copper or wooden surface with emery and water. Into the other end a one-hole rubber stopper is inserted, and pushed in so as to be flush with the opposite end. On the last-mentioned end a perforated platinum disc and a disc of moistened filter paper are placed. Into the hole of the rubber stopper a tube is inserted which is itself connected with the aspirator.

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UNIVERSITY OF MISS., *January* 13, 1887.

On the Oxygen Acids of Iodine.

In an elaborate paper recently published, C. W. Blomstrand shows that the periodates, which are generally regarded as peculiar and inexplicable compounds, are easily understood if they are referred to an acid H_5IO_6 or $IO(OH)_5$. In this compound, and in all the periodates, the iodine is heptavalent. With caustic soda periodic acid forms a salt of the formula $Na_2O_2.IO(OH)_3$, just as phosphoric acid forms the salt $Na_3O_3.PO(OH)$. And just as phosphoric acid forms with silver a salt in which all its hydrogen is replaced by metal—viz. PO_4Ag_3—so periodic acid forms the salt $IO(OAg)_5$ with silver.

The fact that the potassium salt of periodic acid has the composition KIO_4 is explained by assuming that this is a dehydration product of the salt $KO.IO(OH)_4$; thus:

$$KO.IO(OH)_4 - 2H_2O = KO.IO_3.$$

This phenomenon is analogous to that of the formation of sodium pyrophosphate from disodium phosphate:

$$\left.\begin{matrix}Na_2O_2PO.OH\\Na_2O_2PO.OH\end{matrix}\right\} - H_2O = \left.\begin{matrix}Na_2O_2PO\\Na_2O_2PO\end{matrix}\right\} O.$$

The fact that the change in the case of the periodate takes place at ordinary temperatures, while that of the phosphate requires comparatively high heat, is no evidence that the action in the two cases is essentially different.

Ordinary sodium periodate, $Na_2O_2IO(OH)_3$, when heated to 180° to 220° undergoes a change more strictly analogous to that of the phosphate as indicated in the two equations:

(1) $$Na_2O_2IO\left\{\begin{matrix}(OH)_2\\(OH)_2\end{matrix}\right. - H_2O = Na_2O_2IO\left\{\begin{matrix}O\\OH\end{matrix}\right.;$$

(2) $$\left.\begin{matrix}Na_2O_2IO\left\{\begin{matrix}O\\OH\end{matrix}\right.\\Na_2O_2IO\left\{\begin{matrix}OH\\O\end{matrix}\right.\end{matrix}\right\} - H_2O = \left.\begin{matrix}Na_2O_2IO\\Na_2O_2IO\end{matrix}\right\} O = Na_4I_2O_9.$$

The salt $Na_4I_2O_9$ is thus seen to be closely related to ordinary sodium periodate.

Attention is called to the difference between perchloric and periodic acids, a difference which is like that between phosphoric and nitric acids. The normal form of perchloric acid is $HClO_4$ or $HO.ClO_3$, in which the chlorine is probably heptavalent. Evidently chlorine cannot hold in combination as many hydroxyls as iodine can, though both are heptavalent. So, too, in nitric acid the nitrogen is probably quinquivalent $HO.NO_2$, as phosphorus is in phosphoric acid, but the nitrogen cannot hold as many hydroxyls in combination as phosphorus can. A comparison of the formulas will bring this out more clearly:

$HO.NO_2$	$(HO)_3PO$
$HO.ClO_3$	$(HO)_5IO$.

The principal periodates which have been described are those derived from acids belonging to the following series:

(1)	Ortho	$(HO)_5IO$ or $(HO)_2IO(OH)_3$.
(2)	Di	$\left.\begin{matrix}(HO)_4IO\\(HO)_4IO\end{matrix}\right\} O$.
(3)	Meso	$(HO)_3IO.O$ or $\left.\begin{matrix}(HO)_2IO\\(HO)_3IO\end{matrix}\right\} O_2$.
(4)	Dimeso	$\left.\begin{matrix}(HO)_2IO\\(HO)_2IO\end{matrix}\right\} O_2$.
(5)	Meta	$(HO)IO.O_2$.

A number of periodates which have been described are shown to be derived from acids of the above formulas.—(*Journal für praktische Chemie* **34**, 433.)

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

I.—AMERICAN.

ADRIANCE, J. S. Laboratory Calculations and Specific Gravity Tables. New York: Wiley.

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PEALE, A. C. Lists and Analyses of the Mineral Springs of the United States. Bull. No. 32, U. S. Geological Survey.

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JAHRBUCH der Erfindungen und Fortschritte auf den Gebieten der Physik und Chemie, der Technologie und Mechanik, der Astronomie und Meteorologie. Herausgegeben von H. Gretschel und G. Bornemann. XXII. Jahrgang. Leipzig.

KOPP, H. Die Alchemie in älterer und neuerer Zeit. Ein Beitrag zur Culturgeschichte. I. Theil: Die Alchemie bis zum letzten Viertel des 18. Jahrhunderts. II. Theil: Die Alchemie vom letzten Viertel des 18. Jahrhunderts an. Heidelberg.

——— Aus der Molecular-Welt. Eine Gratulationsschrift an Robert Bunsen. 3. Auflage. Heidelberg.

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MENSCHUTKIN, N. Analytische Chemie für den Gebrauch im Laboratorium und für das Selbststudium. Deutsche Ausgabe unter Mitwirkung des Verfassers übersetzt von O. Bach. 2. verbesserte Auflage. Leipzig.

MOHR'S, FRDR., Lehrbuch der chemisch-analytischen Titrirmethode. Neu bearbeitet von A. Classen. Für Chemiker, Aerzte, Pharmaceuten, Berg- und Hüttenleute, Fabrikanten, Agronomen, Metallurgen, Münzbeamte, etc. 6. umgearbeitete und vermehrte Auflage. Braunschweig.

NIETZKI, R. Organische Farbstoffe. 8. Breslau. 165 pp. bd. $1.35.

OSTWALD, W. Lehrbuch der allgemeinen Chemie. II. (Schluss-) Band. Verwandtschaftslehre. 1. Hälfte. Leipzig.

PFEIFFER, E. Die Analyse der Milch. Wiesbaden.

WAGNER, R. v. Handbuch der chemischen Technologie. 12. Auflage. Bearbeitet von F. Fischer. Leipzig.

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